# Defluoridation of drinking water by hybrid coagulation and filtration process

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**Ratnaningtyas Budhi Lestari**

geboren in Jember, Indonesien

Institut für Instrumentelle Analytische Chemie
der
Universität Duisburg-Essen

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Gutachter: Prof. Dr. Torsten C. Schmidt

Prof. Dr. Mathias Ulbricht

Vorsitzender: Prof. Dr. Eckart Hasselbrink

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## Abstract

Fluoride contamination in drinking water can cause severe health problems, namely fluorosis. Defluoridation of drinking water is a practical option to overcome the problem of excessive fluoride in drinking water. Considering that most affected regions are located in less developed countries, it is necessary to find a safe and inexpensive defluoridation technique in order to remove the excess fluoride from drinking water. This study proposes two hybrid methods that have not been investigated with emphasis not only on the fluoride removal but also on the removal of the aluminum residue in the product water.

The first step of the hybrid process is based on coagulation and co-precipitation based on Nalgonda technique. Alum ($Al_2(SO_4)_3$) is used as coagulant, while lime ($Ca(OH)_2$) accounts for maintaining the system pH and as precipitation agent. However, the drawback of this process is a significant aluminum level in the product water.

A systematic process study has shown that the removal of fluoride occurred very fast. It was best carried out at neutral pH and with an excessive amount of aluminum coagulant. Fluoride ions were adsorbed by precipitated aluminum hydroxide. After certain time the precipitated aluminum hydroxide collided and enmeshed fine particles and later settled down. It is suggested that the removal reaction follows a sweep mechanism.

Furthermore, to decrease fluoride concentration to the desired concentration, the optimum alum dosing was successfully determined. Reduction of fluoride concentration from an initial concentration of 10 mg/L to below 1.5 mg/L was best at an aluminum dosing of 100 mg/L that is corresponding to an $Al^{3+}$ to $F^-$ molar ratio $\geq 7$. Meanwhile, for fluoride with initial concentration of 4 mg/L, an $Al^{3+}$ to $F^-$ molar ratio $\geq 4$, equal to 17 mg/L aluminum, achieved the same purpose. This amount of aluminum is clearly lower than needed in the Nalgonda technique which is 16 to 181 mg/L or treating raw water with fluoride levels of 2 to 8 mg/L. Lower amounts of aluminum are preferred to avoid excess of aluminum residue in the product water and to minimize the sludge formation.

A species diagram shows that pH plays the most important role on the process especially in controlling the quality of product water. The removal of fluoride in raw water from the initial concentration of 10 mg/L to below 1.5 mg/L was achieved in the pH range 6 -

8. At this pH range $Al(OH)_3$ has low solubility and easily precipitates. Besides, at this pH the $pH_{PZC}$ of $Al(OH)_3$ indicates that the precipitate is neutral to positively charged. In addition, by maintaining the pH on this level, the amount of $OH^-$ ions as competing ion to fluoride to occupy $Al(OH)_3$ precipitate is also smaller.

As second step in the hybrid process a sand filter has been investigated to deal with excess residue of aluminium in the produce water. The insertion of a sand filter after the coagulation and co-precipitation step is proposed considering that the high level of aluminium in the product water is caused by suspended aluminium that still remained in product water after long term of settling down. In the laboratory scale, sand filtration as part of the hybrid process showed successful removal of aluminium to a concentration that will not lead to a risk for consumer health based on WHO standard (0.2 mg/L).

Finally, a hybrid process of coagulation and co-precipitation with membrane ultrafiltration has been investigated. The hybrid process also successfully achieved 90% reduction of aluminum concentration in the water after the coagulation and co-precipitation step by the UF membrane operation. The aluminum concentration after the hybrid process fulfilled the WHO standard of 0.2 mg/L.

In conclusion, the study on the hybrid proces coagulation and co-precipitation with filtration for defluoridation of drinking water has brought a new insight on how to control the coagulation and co-precipitation process. Extention to this work by using additional parameter gives a new opportunity on its development. The investigation has also shown that the hybrids defluoridation process is considerable technique that can be applied as alternatives to the existing one. Investigation to different material of membrane will open a new challenge in its application.

# Kurzfassung

Fluorid verunreinigung im Trinkwasser kann schwere gesundheitliche Probleme verursachen, nämlich Fluorosis. Fluoridentfernung von Trinkwasser ist eine praktische Möglichkeit, um das Problem zu beseitigen. Aufgrund dessen, dass die meisten betroffenen Regionen weniger entwickelten Ländern sind, ist es notwendig, eine sichere und kostengünstige Technik zu finden, um das überflüssige Fluorid aus Trinkwasser zu entfernen. Diese Studie bittet zwei Hybridmethoden, die nicht nur auf die Fluoridentfernung konzentrieren, sondern auch auf die Entfernung des Aluminiumrücktstand im Produktwasser.

Die ersten Maßnahmen des Hybridsverfahrens enstanden durch Koagulation und Mitfällung, eine Technik, die auf sogenannte Nalgonda Technik basiert. Als Koagulationsmittel wird Alaun ($Al_2(SO_4)_3$) verwendet, während Kalkmilch ($Ca(OH)_2$) für die Pflege des pH-Wertes des Systems und als Fällungsmittel verantwortlich ist. Der Nachteil dieses Verfahrens ist jedoch ein signifikanter hohe Aluminiumgehalt im Produktwasser.

Diese Studie zeigte, dass die Entfernung von Fluorid sehr schnell auftrat. Es wurde am besten bei neutralem pH-Wert und mit einer übermäßigen Menge an Aluminium als Koagulationsmittel durchgeführt. Fluoridionen wurden durch ausgefällte Aluminiumhydroxid absorbiert. Nach einer gewissen Zeit, kollidierte das ausgefällte Aluminiumhydroxid zusammen und verästelte feine Teilchen und setzte sich später nieder. Es wird vorgeschlagen, dass die Entfernungsreaktion einem Sweep-Mechanismus folgt.

Weiterhin wurde in dieser Studie die optimale Aluminiumdosierung erfolgreich ermitteln, um die Fluoridkonzentration auf die gewünschte Konzentration zu reduzieren. Die Reduktion der Fluoridkonzentration von einer Initialskonzentration von 10 mg/L bis unter 1,5 mg/L war am besten bei einer Aluminiumdosierung von 100 mg/L, die einem $Al^{3+}$ zu $F^-$ Molverhältnis ≥ 7 entspricht. Dieses Molverhältnis sichert eine hohe Möglichkeit zur Fluoridadsorption an Aluminiumhydroxidpräzipitaten als Adsorptionsstellen. Diese Menge an Aluminium ist deutlich niedriger als die, die in der Nalgonda-Technik verbraucht ist. Diese entspricht 16 bis 181 mg/L für zur Behandlung für eine von 2 bis 8 mg/L Fluoridekonzentration in Rohwasser. Selbsverständlich, geringere Mengen an Aluminium

werden bevorzugt, um einen Überschuss an Aluminiumrest im Produktwasser zu vermeiden und die Schlammbildung zu minimieren.

Die in der Studie ausgebildet Speziesdiagrammen zeigte die deutlich, dass der pH-Wert die wichtigsten Rolle bei dem Prozess spielt, insbesondere bei der Kontrolle der Qualität des Produktwassers. Die Entfernung von Fluorid in Rohwasser aus der Initialskonzentration von 10 mg/L bis unter 1,5 mg/L erreichte pH-Bereich von 6 bis 8. Bei diesem pH-Bereich hat Aluminiumhydroxid eine geringe Löslichkeit und fällt leicht aus. Darüber hinaus ist die Menge an OH-Ionen als konkurrierende Ionen zu Fluorid, um eine $Al(OH)_3$ Präzipität zu besetzen, ebenfalls geringer, wenn der pH auf diesem Niveau gehalten wird.

Als zweiter Schritt im Hybridverfahren wurde ein Sandfilter untersucht, um mit überschüssigem Aluminiumrückstand im Produktwasser umzugehen. Das Einfügen eines Sandfilters nach dem Koagulations- und Mitfällungsschritt wird vorgeschlagen, da der hohe Aluminiumgehalt im Produktwasser durch suspendiertes Aluminium verursacht wird, das jedoch nach längerem Absetzen in Produktwasser verblieb. Im Labormaßstab führte die Sandfiltration als Teil des Hybridverfahrens zu einer erfolgreichen Entfernung von Aluminium zu einer Konzentration, die nicht zu einem Risiko für die Verbrauchergesundheit auf der Grundlage des WHO-Standards (0,2 mg/L) führt. Schließlich wurde noch ein hybrides Verfahren nämlich der Koagulation und Mitfällung mit Membran-Ultrafiltration untersucht. Das Hybridverfahren, durch den UF-Membranbetrieb, führte zum einen erfolgreichener Betrieb, wo er bis zu einer 90% Reduktion der Aluminiumkonzentration, die im Wasser nach dem Koagulations- und Mitfällung verbleibt, erfolgte. Die Aluminiumkonzentration nach dem Hybridverfahren erfüllte den WHO-Standard von 0,2 mg/L.

Schlussendlich die Hybridsverfahren Studie mit dem Einsatz von Koagulation und Co-Präzipitation mit Filtration zur Defluoridierung von Trinkwasser gewährte einen neuen Einblick in die Steuerung des Koagulations- und Co-Präzipitationsprozesses. Die Erweiterung dieser Arbeit durch die Verwendung von zusätzlichen Parametern bietet eine neue Chance für ihre Entwicklung. Die Untersuchung zeigte auch, dass das Hybridsverfahren eine bedeutungsvolle Technik ist, die als Alternative zu dem bestehenden angewendet werden kann. Die Untersuchung verschiedener Membranmaterialien eröffnet eine neue Herausforderung in ihrer Anwendung.

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# Chapter 1 General Introduction

## 1.1 Fluoride and fluorosis

Fluoride, as a common dissolved constituent of drinking water, causes either beneficial or adverse health effects on the consumer depending on its concentration. Intake of fluoride in excess amounts most commonly through drinking water can cause fluorosis that affects teeth and bones health. Millions of people are exposed to excessive amounts of fluoride through contaminated drinking water caused by natural geological sources.

Fluorosis is a chronic disease manifested by mottling of teeth in mild cases (dental fluorosis) and softening of bones, ossification of tendons and ligaments, and neurological damage in severe cases (skeletal fluorosis) [1]. Therefore, when the levels of fluoride in drinking water are above the standard limit set by the World Health Organisation (WHO) to 1.5 mg/L, there might be an increased risk of fluorosis. Children are most at risk because they are still in the growing age. It is estimated that around 200 million people, from 25 nations over the world, suffer from fluorosis [2]. India and China, the two most populous countries of the world, are the worst affected. Figure 1-1 highlights countries with reported cases of fluorosis incidents [3].

Fluoride is the ionic form of fluorine ($F_2$), which in aqueous solution forms $F^-$ ions. Fluorine is the most electronegative and the most reactive chemical element. It has a strong tendency to acquire a negative charge. Therefore, it is almost never found as fluorine in the environment but as fluoride. In earth's crust, fluoride is significantly abundant with an average of 625 mg/kg and mostly retained in minerals because of its low mobility in aqueous environments [4]. Fluoride forms minerals with a number of cations and some mineral species of low solubility contain fluoride, for instance fluorite ($CaF_2$).

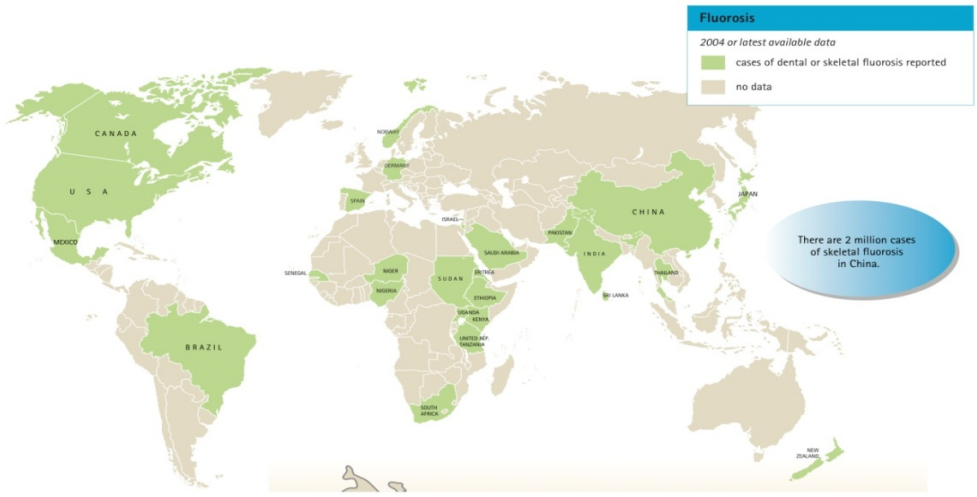


**Figure 1-1 Reported endemic cases of fluorosis, adapted [5]**

In the environment, fluoride is commonly found in the lithosphere mainly as fluorspar, rock phosphate, cryolite, apatite, mica and hornblende [6]. In seawater, fluoride concentrations reach around 1.2 – 1.4 mg/L, in ground waters up to 67 mg/L and in most surface waters less than 0.1 mg/L [7]. The hydrogeochemical cycle of fluorine is illustrated in Figure 1-2.

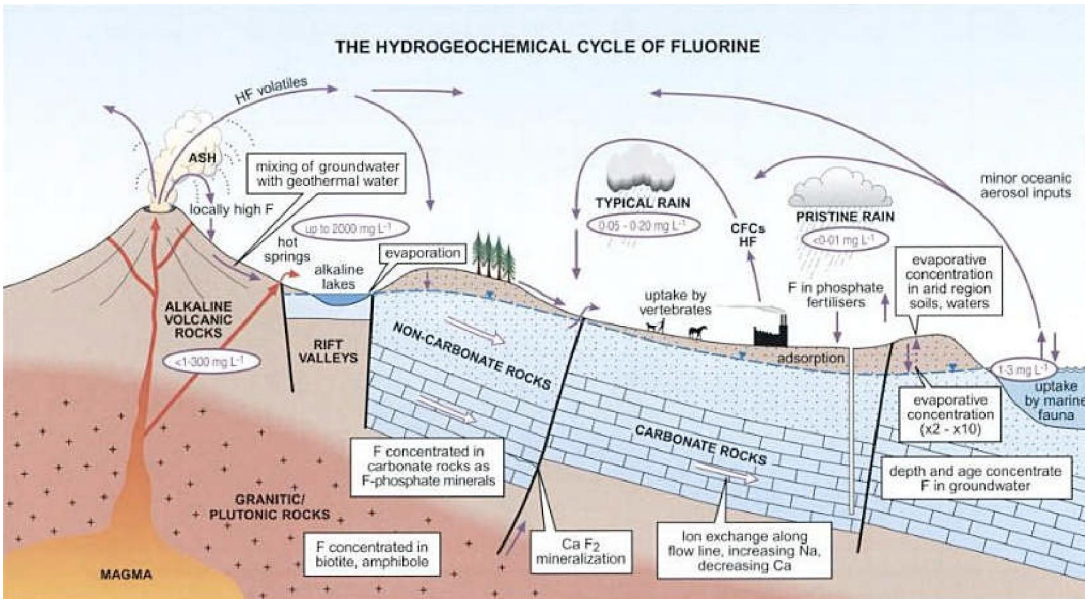


**Figure 1-2 Illustrated hydrogeochemical cycle of fluorine, adapted [8].**

Water with high fluoride concentration is usually found at the foot of high mountains, and in areas with geological deposits of marine origin. Typical examples are the geological belt from Syria through Jordan, Egypt, Libya, Algeria, Morocco and the Rift Valley. Another belt is the one stretching over India, northern Thailand and China. Similar areas can be found in the Americas and in China and Japan [3].

Fluoride is also found at elevated concentrations near to places where volcanic activity exists, especially with the emission of fumarolic gases through fumaroles. Fumaroles are vents in the earth crust that emit steam and gases. The interaction of volcanic gas with high temperature (600 – 700 °C) rock wall forms acidic condensate. This condensate has low pH and is rich in halogen content after escape through fumaroles with a sudden pressure drop. After condensation and oxidation, the rock becomes a halogen rich mineral, including fluoride [9]. Thermal waters often found in volcanic areas are also rich in fluoride, especially those with high pH [4]. Some fluoride minerals are categorized as industrial raw material including cryolite ($Na_3AlF_6$), which is used for the production of aluminum and pesticides [6]. Sodium fluoride (NaF) is a source of fluoride that is added to toothpaste in order to protect teeth against dental caries. The following Table 1-1 summarizes reported elevated fluoride concentrations in several areas in the world.

**Table 1-1 Reported elevated fluoride concentrations in water in some endemic areas in the world**

| Location (area in) | Detected Fluoride Concentration (mg/L) | Type of water | References |
|---|---|---|---|
| Northern Cape, South Africa | 30 | Ground water | [10] |
| Agra, India | 210 | Ground water | [11] |
| Rift Valley, Ethiopia | 26 | Ground water | [12] |
| United Rep. Tanzania | 95 | Ground water | [13] |
| Lake Nakuru, Kenya | 2800 | Surface water | [14] |
| Ijen (crater) Lake, Indonesia | ~1500 | Surface water | [15] |
| Chihuahua, Mexico | 5.9 | Ground water | [16] |
| El Paso, TX, USA | 4.8 | Ground water | [16] |

Fluoride present in drinking water is considered an important source for the human body. Fluoride is also present in some foods in significant concentrations. Table 1-2 shows some foods with substantial fluoride contents.

**Table 1-2 Fluoride concentrations in some foods and beverages**

| Food/beverage | Fluoride concentration | References |
|---|---|---|
| Barley and Rice | ~2 mg/kg | [17] |
| Meat in general | 0.2 – 1 mg/kg | [17] |
| Fish | 2 – 5 mg/kg | [17] |
| Fish protein concentrate | ~ 370 mg/kg | [17] |
| Vegetable and fruit | 0.1 – 0.4 mg/kg | [17] |
| Human breast Milk | < 0.02 mg/L | [6] |
| Cow's milk | 0.02 – 0.05 mg/L | [18], [18] in [6] |
| Tea leaves (dry weight) | 400 mg/kg | [6] |
| Tea (infusion) | 0.5 – 1.5 mg/L | [6] |
| Fresh fruit juice | 0.3 – 0.5 mg/L | [6] |
| Beer | 0.3 – 0.8 mg/L | [6] |
| Wine | 6 – 8 mg/L | [6] |
| Cereal | 4.2 mg/kg | [13] |

Fluoride plays an important role in the development of teeth enamel in young children and strengthening the bone matrix. Bones and teeth consist mainly of apatite, that is composed of a mixture of hydroxyapatite (HAP), ($Ca_{10}(PO_4)_6$ $(OH)_2$) and fluorapatite (FAP), ($Ca_{10}(PO_4)_6F_2$). $F_2$ and $(OH)_2$ in these compounds are interchangeable. Due to the dietary behaviour in fluoride consumption, the ratio of FAP to HAP in human teeth and bones can be very low. This leads to easily soluble teeth material under acidic condition that in the dental practice is called dental caries. On the contrary, a high ratio of FAP to HAP can cause fluorosis [19].

WHO supports the hypothesis that the prevalence of dental caries is antiproportionally related to the concentration of fluoride in drinking water [3] Since the discovery of the caries-preventive effect of fluorides in the 1930's, different forms of fluoride administration programs have been implemented. Fluoride has been added to different media such as water, salt, toothpaste, and milk [20,21].

Later, it was suggested that excess in fluoride uptake may lead to harmful effects on the human body and that there is a relationship between the concentration of fluoride in drinking water and the prevalence of dental fluorosis [15]. In the range of 0.8 to 1.2 mg/L, fluoride is considered to be effective in preventing dental caries, but concentrations higher than 1.5 mg/L are reported to be harmful [22]. A study in Asembagus, Indonesia, suggested that the risk for dental fluorosis is already increased at only 0.5 mg/L fluoride in drinking water and that 1.1 mg/L fluoride may cause skeletal fluorosis [15]. This shows that climate, drinking and dietary behaviour may determine the need or danger of fluoride uptake through drinking water.

The dental effects of fluorosis develop much earlier than the skeletal effects in human beings when they are exposed to large amounts of fluoride. Symptoms can develop with regular consumption of water containing fluoride concentrations as low as 1 to 2 mg/L [1]. Dental fluorosis typically can be seen as staining and pitting of the teeth. In more severe cases, all the enamel may be damaged. Children are particularly sensitive during the years of teeth formation. During the growth phase of the skeleton, a relatively high fraction of an ingested fluoride dose will be deposited in the skeleton. Long-term intake of large amounts and chronic high-level exposure to fluoride can lead to potentially severe skeletal fluorosis because fluoride accumulates in the bones progressively over many years.

## 1.2 Water defluoridation

Water defluoridation is one of the options available to prevent fluorosis endemic in areas that have high concentrations of fluoride in their water sources. From previous studies, water defluoridation methods can be categorized into three groups, namely coagulation and precipitation, adsorption, and membrane processes as shown in Figure 1-3. The main purpose in water defluoridation is to reduce the fluoride concentration to the permissible level set by WHO to 1.5 mg/L. The following section discusses selected methods and techniques on defluoridation.

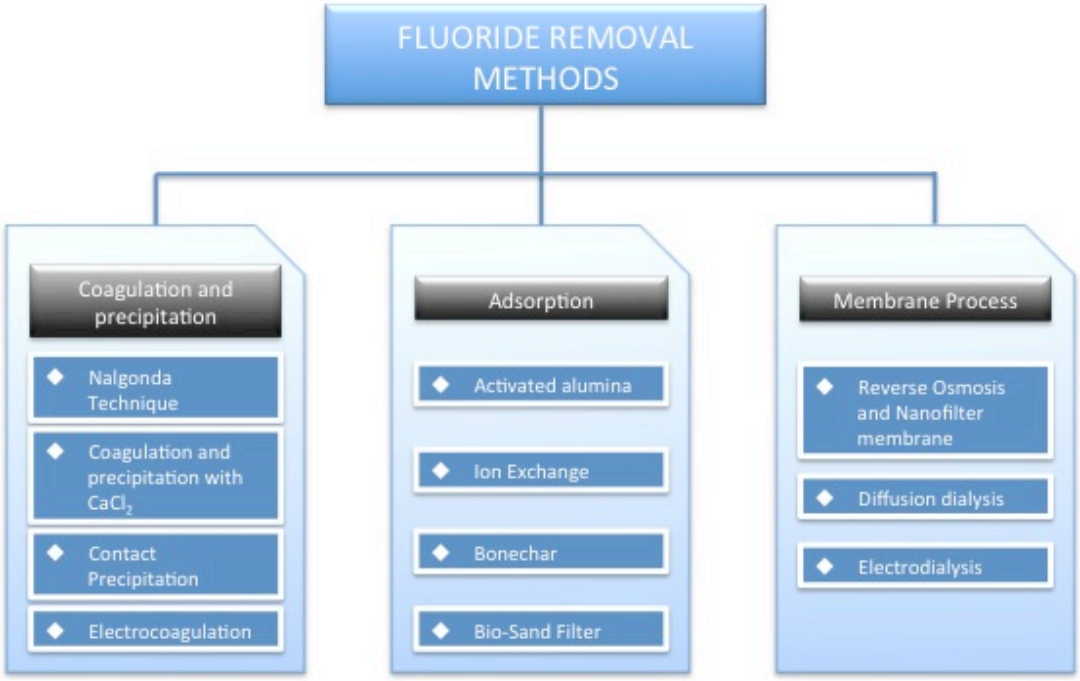


**Figure 1-3 Overview of fluoride removal methods**

### 1.2.1 Nalgonda technique

One of the applicable techniques to remove excessive fluoride from water is coagulation and precipitation. Lime ($Ca(OH)_2$) and alum ($Al_2(SO_4)_3$) are the most commonly used coagulants. The Nalgonda technique is one of the most studied in this category. It is named after the Nalgonda area in India where fluorosis is widespread. This technique was developed by the National Environment Engineering Research Institute (NEERI) Nagpur, India after extensive testing of many materials and processes [23,24]. The Nalgonda technique involves addition of alum and lime followed by mixing, flocculation, precipitation, sedimentation and disinfection.

The first removal process occurs through precipitation following lime dosing

$$2NaF_{(aq)} + Ca(OH)_{2(aq)} \rightarrow 2Na(OH)_{(aq)} + CaF_{2(s)} \quad (1)$$

This process will lead to the precipitation of calcium fluoride and usually raise the water pH up to 12. Some reports show that by only lime dosing it was possible to reduce fluoride concentrations from 10 mg/L to 8 mg/L [1,23,25]. By adding alum into the water, coagulation is facilitated. When alum is added to water, essentially two reactions occur. In the first reaction, alum reacts with some of the hydroxide to produce insoluble aluminum hydroxide

[$Al(OH)_3$] as the active surface of fluoride adsorption. In the second reaction, aluminum ions react with fluoride that is still present in the water to form fluoride complexes and aluminum hydroxyl fluoride [24]. The reactions can be described as follows:

Aluminum precipitation:

$$2Al^{3+} + 6H_2O \rightarrow 2Al(OH)_3 + 6H^+ \quad (2)$$

Co-precipitation:

$$F^- + Al(OH)_3 \rightarrow Al\text{–}F \text{ complex} + \text{undefined product} \quad (3)$$

Compared to common drinking-water coagulation and flocculation, a larger dosage of alum is normally required in the defluoridation process. In practice, 16 – 181 mg/L Al is needed to treat raw water with fluoride levels of 2 – 8 mg/L [24]. Coagulation is carried out by rapid stirring, while flocculation is facilitated by slow stirring. The process continues with sedimentation. The best fluoride removal is accomplished by using alum as coagulant at a neutral pH range 6.5 – 7.5 [26]. As it is shown in Figure 1-4 solubility of aluminum is minimized at neutral pH based on the solubility diagram of α-$Al(OH)_{3(s)}$ [27].

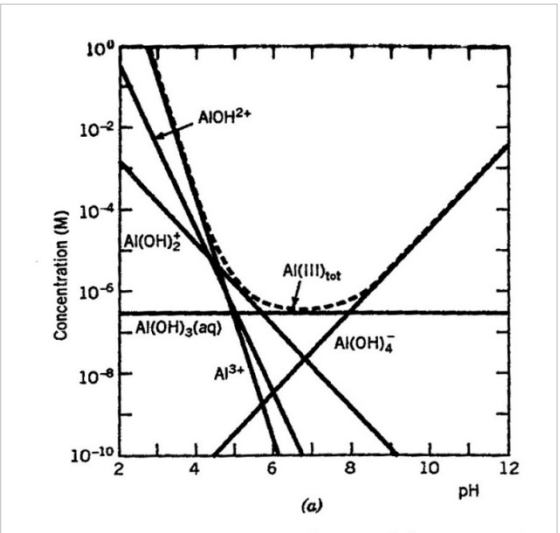


**Figure 1-4 Solubility diagram of α-$Al(OH)_{3(s)}$ [27]**

The involved chemicals in this technique are fairly regular. After years of experience, some improvements have been made to adapt with the local community factor. The needed chemicals are already prepared in particular packaging with properly dosage to avoid

miscalculation. The Nalgonda technique is also reported to be adaptable to drinking water equipment such as hand pumps [23,28].

However, aluminum and lime dosage depend on the initial concentration of fluoride in the water. Thus a concentration test has to be done before treating the water. Wrong dosage of alum will lead to inappropriate pH of the water [29]. Inappropriate pH of the water will lead to ineffective treatment and can cause the formation of $Al^{3+}$, $Al(OH)^{2+}$, $Al(OH)_2^{+}$ that are dissolved in water and toxic to humans, thus eliminating the benefit of the technique [30].

Previous studies suggested that the residual aluminum, which may reach concentrations above 0.2 mg/L, the threshold limit value set by WHO, under certain circumstances could cause several potential health risks to humans. Excess of aluminum concentrations in drinking water is suspected to have an effect on cognitive decline [31]. Excessive aluminum uptake is also believed to increase prevalence of Alzheimer disease [30,32,33]. Besides that, due to the use of aluminum sulfate as coagulant, the sulfate ion concentration increases tremendously, and in few cases, it exceeds the maximum permissible limit of 400 mg/L, which may cause cathartic effects in human beings [23].

Another disadvantage is that treated water has a specific taste due to chemicals addition. Since the water matrix may change over time and season, regular analysis of feed and treated water is required to calculate the correct dose of chemicals to be added. As the process involves an excessive amount of aluminum sulfate as coagulant, this technique results in formation of large volumes of sludge. Therefore, large space is required for drying the sludge and its disposal that lead to additional cost for it.

### 1.2.2 Coagulation and precipitation using calcium chloride

Recently, calcium chloride (CC) has become an alternative to lime addition prior to the coagulation with aluminum coagulant in the fluoride removal process. CC is preferred over lime because it produces less sludge than lime [34]. CC will precipitate with fluoride forming $CaF_2$. But as discussed in the previous section, precipitation alone is not sufficient to remove fluoride to concentrations below 1.5 mg/L. Higher CC dosage leads to increased water hardness. CC is usually being applied in wastewater treatment plants treating fluoride rich wastewater such as from glass, ceramic and semiconductor industries. However, there are

still drawbacks on its application such as very fine precipitation of $CaF_2$ requiring longer time for sedimentation.

### 1.2.3 Contact precipitation

Contact precipitation is a practicable technique for defluoridation in less developed countries. It is mostly applied in Africa. This technique could remove fluoride from water through the principle of adsorption of fluoride by bone char and precipitation by the addition of calcium chloride and monosodium phosphate (MSP) in a column bed [35]. Bone char consists mostly of hydroxyapatite ($Ca_5(PO_4)_3OH$) and the percentage of hydroxyapatite varies depending on its calcination process. At first, the column is saturated with water to avoid the formation of air bubbles that will reduce the removal level.

The removal of fluoride works in two ways. First, adsorption of fluoride takes place on the active surface of hydroxyapatite, after the release of $OH^-$ ions. Second, calcium chloride and MSP dissolve as they are contacted with water. In those two processes calcium fluoride and fluorapatite are formed [36]. In case of the use of calcium phosphate pellets, precipitation occurs as the pellets slowly release calcium and phosphate ions when they are contacted with water. The reactions is suggested to occur as follows [17] :

Dissolution of calcium chloride:

$$CaCl_2.2H_2O_{(s)} \rightarrow Ca^{2+} + 2\ Cl^- + 2H_2O \quad (4)$$

Dissolution of MSP

$$NaH_2PO_4.H_2O_{(s)} \rightarrow PO_4^{3-} + Na^+ + 2\ H^+ + H_2O \quad (5)$$

Precipitation of calcium fluoride:

$$Ca^{2+} + 2\ F^- \rightarrow CaF_{2(s)} \quad (6)$$

Precipitation of fluorapatite:

$$10\ Ca^{2+} + 6PO_4^{3-} + 2\ F^- \rightarrow Ca_{10}(PO_4)_6F_{2(s)} \quad (7)$$

It has been concluded that the contact bed also acts as deep bed filter for the suspension of fine precipitate [37]. The optimum contact time is the critical point for this

technique. Though it is reported that 20 to 30 minutes of contact time had shown an excellent result, previous studies failed to determined the optimum contact time [17]. Too short contact time leads to reduction in **removal capacity** and too long contact time will minimize **removal efficiency**. The major issue for the scale up application is the lifetime of the filter and maintenance due to the continuous supply of calcium and phosphate. As mentioned above, the potential utilization of bone char also needs to take into account local beliefs in specific region.

### 1.2.4 Electrocoagulation

Electrocoagulation (EC) is commonly used to remove fluoride from industrial wastewater [38]. Some industries, e.g. coke manufacture, electronics and semiconductor manufacture, electroplating operations, steel, glass and aluminum manufacture, metal etching, wood preservatives, and pesticide and fertilizer manufacture discharge significant quantities of fluoride containing wastewater in form of hydrogen fluoride (HF) or fluoride ions ($F^-$), depending upon the pH of the waste [25,39]. Beside fluoride, the wastewater typically also contains heavy metals, phenol, and other organic chemicals.

EC was also applied to remove fluoride from drinking water [40]. In EC the aluminum sorbent is generated electrochemically using a sacrificial electrode as an alternative to the conventional alum addition or treatment with activated alumina. The method principle is shown in Figure 1-5. As the electric current passes through the anode, the aluminum electrode is oxidized to aluminum ions. After that, aluminum ions are transformed to polymeric species or $Al(OH)_3$ flocs, which can co-precipitate or adsorb the fluoride ions [41].

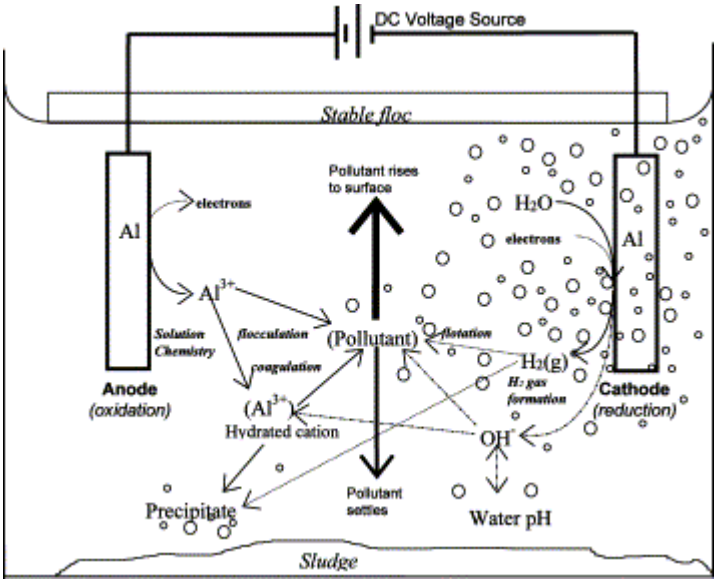


**Figure 1-5 Illustration of interactions occurring within an electrocoagulation reactor [42]**

Nevertheless, the kinetic of this method is still under debate with two opposite opinions. Each opinion supports their finding with laboratory data. One side suggested that the defluoridation rate of the EC process is a first-order reaction with respect to fluoride concentration [43,44]. The reaction kinetics is described as follows:

$$F_t^- = [F_0^-].e^{(-k_1 t),}$$

where:

$F_t^-$ = fluoride concentration at time t

$F_0^-$ = initial fluoride concentration

$k_1$ = first-order rate constant

t = reaction time.

On the other hand, there is a different interpretation of the experimental results [41]. Because their results demonstrated that k1 declines as the initial fluoride concentration rises, they concluded that the reaction could not be a first order reaction. The k1 in a first order reaction must not change with the initial fluoride concentration. The defluoridation of the EC process, therefore, should be a pseudo-first-order reaction.

Another study reported that freshly generated Al-sorbent is able to reduce fluoride concentration from 16 to 2 mg/L in 2 minutes [25]. However, in that experiment the

adsorption of fluoride ions on Al-sorbent reaches equilibrium at 2 mg/L of fluoride concentration throughout the 12 minutes treatment. This prevented the adsorption process to further reduce the fluoride concentration to less than 1.5 mg/L. Besides, the presence of sulfate ions led to lower defluoridation efficiency [45].

### 1.2.5 Activated alumina

Activated alumina is one of the most frequently used adsorbents to remove fluoride from drinking water. Activated alumina that commonly refers to γ-$Al_2O_3$ is created from the dehydroxylation of aluminum hydroxides. Activated alumina has very high surface area to weight ratio due to many pores s that is formed during the formation. The BET surface of γ-$Al_2O_3$ is known to be 174 - 192 $m^2/g$, depending on its calcination temperature [46]. The mechanism of fluoride removal, although not fully clear, is based on the electrostatic interaction between the fluoride ion and the positive surface charge of alumina ($pH_{pzc}$ 9.5) [27]. Furthermore, its removal efficiency is affected by total surface area, surface charge, pH condition, and also the number of available adsorption sites on the media surface as well as crystalline structure. Different crystalline structures of alumina will lead to different binding energy capacity to interact with fluoride ions [27].

The pH condition plays a role on dissolution effect of the compounds in water that will lead to the release of both aluminum and fluoride ion into the water. Studies show that the point of zero charge ($pH_{pzc}$) is in the pH range of 6.2 to 9.6 [47-49]. When pH is above the $pH_{pzc}$, fluoride sorption decreases due to the electrostatic repulsion between the alumina's surface and fluoride anions due to the net negative surface charge of alumina. In addition, hydroxide ions become stronger competitors to the fluoride ions for occupying the active sites on activated alumina. At pH below $pH_{pzc}$, it is reported that fluoride removal might reach up to 94% [50]. Several studies give a good agreement on the optimum pH range for fluoride adsorption on alumina between pH 5 to 6 [47] [48]. At pH below 5, the solubility of alumina increases and when alumina is dissolved, the sorbed fluoride will be released [51]. Therefore this method is sensitively pH dependent.

Though adsorption with activated alumina was suggested as relatively save and efective method, still there is another challenge on its application namely regeneration. Different

grade of activated alumina has different lifetime. Monitoring of water quality has to be performed in order to control if the adsorbent is saturated and has to be regenerated.

### 1.2.6 Ion exchanger

It is reported that fluoride removal by using anion-exchange resins is very complex considering the order of selectivity for anionic species by comercially available anion exchange resins. The selectivity is as follows: citrate > $SO_4^{2-}$ > oxalate > $I^-$ > $NO_3^-$ > $CrO_4^{2-}$ > $Br^-$ > $SCN^-$ > $Cl^-$ > formate > acetate > $F^-$ [52].

From the list above, it can be seen that fluoride has the least selectivity while citrate has the highest selectivity. Due to the low selectivity for fluoride, anion exchangers are less considered to remove fluoride from drinking water. Therefore, several studies have examined modified cation exchangers for fluoride removal (see below). Research work on fluoride removal has been carried out using metal doped cation exchangers such as lanthanum (III) [53]. In addition, inorganic cation exchangers such as silica gel [54] and alumina gel has also been studied [55].

By anion-exchange resin, the removal can be described as the following ion exchange mechanism [23,56]:

$$Resin\text{-}NR_3{+}Cl^- + F^-_{(aq)} \rightarrow Resin\text{-}NR_3{+}F^- + Cl^- \quad (8)$$

The fluoride ions replace the chloride ions of the resin until the equilibrium is reached. The resin is regenerated by backwashing with water that is supersaturated with dissolved sodium chloride salt. Regenerated chloride ions will replace the fluoride ions and lead to recharge of the resin.

Cation-exchanger resin dopped with metal ions e.g. Aluminum, Iron, Lanthanum, etc removes fluoride with similar mechanism as adsorption mechanism. The mechanism can be described as follow:

$$Resin\text{-}SO_3H + F^-_{(aq)} \rightarrow Resin\text{-}SO_3H^{\delta+ \cdots F^{\delta-}} \quad (9)$$

Due to H-bonding, the selectivity of fluoride in cation exchangers is higher than the other ion. The preference of adsorption of anions is supposed to be in the following order: $F^-$ > $Cl^-$ > $NO_3^-$ > $SO_4^{2-}$.

Nevertheless, ion exchanger has drawbacks in its utilisation. First, it requires trained operators due to its advanced technique, maintenance, and data interpretation. Second, the concentrated fluoride waste from resins regeneration needs to be treated separately before final disposal. Third, the treated water has a low pH and high level of chloride that needs to be polished before being consumed. Furthermore, synthetic resins are not an economically viable option for less developed countries [1,57].

### 1.2.7 Bone char

The application of bone char in the water treatment process to remove fluoride has been known for decades [57]. This method is based on the sorption of fluoride by charred bone. Modification of the process by adding brushite ($CaHPO_4 \cdot 2H_2O$) and calcium hydroxide to improve the efficiency of the bone char method was investigated [58]. The addition of brushite leads the increase of bone char adsorption to the maximal until it reach supersaturated condition and formed fluorapatite. It was found that the fluoride removal increases 20 times compared to the process without addition of brushite. Many investigations have been done on the sorption capacity of bone char which was mainly obtained from pyrolysis of cattles bone [57,59] and from fish bone [60]. Another study proposed the mechanism of the fluoride removal by bone char is caused by exchange between phosphate ions in the charred bone with fluoride ions in the treated water and it is endothermic [61].

It has been reported that more than 700 L of water with initial fluoride concentration of 12 mg/L can be filtered to below the WHO standard of 1.5 mg/L by a bone char column of height 50 cm and diameter 15 cm (equivalent to > 80 filter bed volumes) [62]. However, bone char efficiency may decrease if the product water is withdrawn at the high rate. In addition, as an adsorbing medium, renewal of bonechar is needed when it is saturated. However, attempts to predict the saturation point failed so far. Therefore, monitoring needs special attention [17]. Besides, the origin of the bone could be of interest for some groups of people considering their faith. For instance, Muslims will not use charred bone that came from swine, as well as Hindus that will not use charred bone from cattle.

### 1.2.8 BioSand filter (BSF)

The BioSand Filter (BSF) is a biological filter that utilises the biological activity coupled with continuously operated slow sand filtration processes to the household level. The BSF's biological filtration, applied physical filtration, adsorption by the sand particles as well as the formation of a living layer in the upper most layers of sand. This microorganism layer that is particularly dense in about the top 1-3 cm is known as the bio-layer. The original purpose of BSF was to remove turbidity and bacteria. Previous studies suggested that BSF operated at flow rate of 15 and without any modification for fluoride removal indicated that no fluoride removal and or no consistent result in the experiments [63] or 20 L/h are able to remove turbidity up to 1 NTU [43,44].

Modification with zeolites were investigated to remove fluoride, and the result indicated 54% of fluoride has been removed from water [64]. While an adaptation of BSF using lateritic clay, local brick and bonechar were investigated, only adaptation with bonechar as filter media was able to remove fluoride from 8.6 mg/L to meet the WHO limit of 1.5 mg/L. However, it was concluded that the filter media are easily exhausted and pretreatment has to be performed [65].

### 1.2.9 Membrane clasification

Nowadays, membrane processes have emerged as a preferred alternative to provide safe drinking water with minimum problems associated with other conventional methods such as excessive mineral content, hygienic problems from the presence of microorganisms, etc. There are several types of membranes that are classified by their structure, which can be homogeneous, heterogeneous, symmetric or asymmetric; by their nature, biological or synthetic; and according to the nature of the transport, active or passive. Synthetic membranes can also be divided into organic (polymeric or liquid) and inorganic (ceramic or metal). Table 1-3 shows a general classification of membranes and exemplary applications.

**Table 1-3 Selected type of membrane separation processes based on driving force and separation mechanism [66]**

| Membrane process | Membrane barrier | Driving force | Separation mechanism | Example |
|---|---|---|---|---|
| Microfiltration (MF) | Porous (d > 100 nm) | P | Size exclusion (sieving) | Sterile filtration of aqueous solutions |
| Ultrafiltration (UF) | Porous (d < 100 nm) | P | Size exclusion (sieving) | Concentration of biomacromolecule solutions |
| Nanofiltration (NF), aqueous | Nonporous or microporous, charged | P | Solution-diffusion Donnan exclusion | Removal of bi-/multivalent ions from water |
| Reverse osmosis (RO) | Nonporous polymer | P | Solution-diffusion | Ultrapure water production |
| Electrodialysis (ED) | Nonporous or porous | E | Solution-diffusion, size exclusion or charge exclusion | Water desalination, |

Porous membranes are used for MF and UF processes, and their principle is physical separation. NF membranes have pores in the nanometer scale range, between the range of UF and RO, and RO membranes theoretically have no pores, though in practice there are small manufacture defects that result in pore formation. In RO, process separation takes place by the principle of diffusion through the membrane. Figure 1-6 illustrates the comparative size of the membrane pore and diameter of some substances.

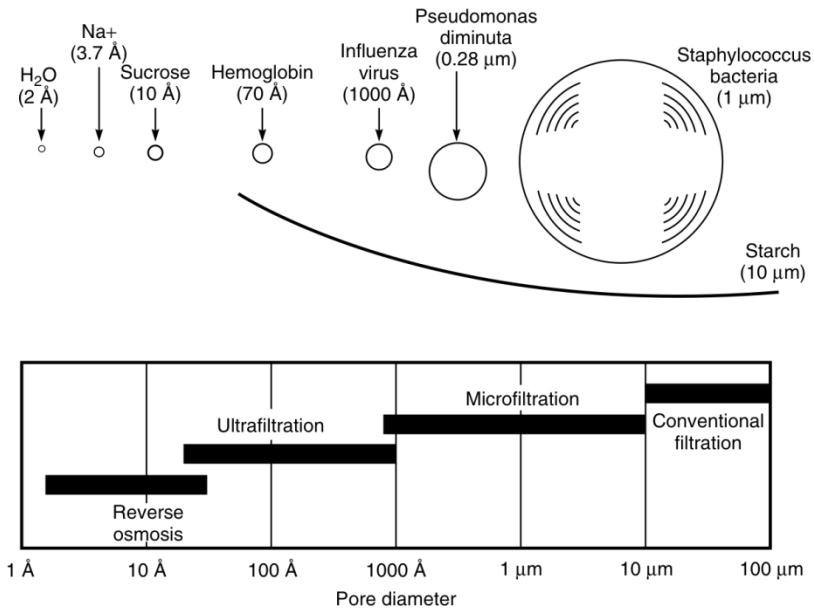


**Figure 1-6 Pore diameter of membrane [67]**

The efficiency of a membrane is determined by its selectivity and the flux through the membrane. Selectivity is the capacity of the membrane to retain some particles and let others pass. This is normally expressed as Retention (R) that is given by:

$$R = \frac{C_f - C_p}{C_f} = 1 - \frac{C_p}{C_f}$$

where:

R = retention, dimensionless [-]

$C_p$ = solute concentration in the permeate [w/v]

$C_f$ = solute concentration in the feed [w/v]

### 1.2.10 Reverse osmosis and nanofiltration

Not all membrane types that were mentioned in the previous section are able to remove fluoride directly. There are two types of membranes that can remove fluoride directly from water: nanofiltration (NF) and reverse osmosis (RO). NF is operated at lower pressure compared to RO and removes primarily the larger suspended solids. RO is operated at higher pressures with greater rejection of ions. Many researchers have documented fluoride removal efficiencies up to 98% by membrane processes [68-73]. RO is usually utilised in desalination processes to treat salt water to drinking water. RO is the reverse process of natural osmosis. Pressure is applied to overcome the natural osmotic pressure. The RO membrane rejects ions based on size and electrical charge.

Beside fluoride, RO and NF can also remove suspended solids, organic and inorganic pollutants, pesticides and microorganisms, etc. If the water characteristic is already known and pre-treatment is provided, the life of membrane might be longer compared to a process without pre-treatment. In addition, membranes work at a wide pH range. RO is applied extensively in desalination industry. However, in general water treatment process, NF is suggested to be more suitable over RO for future applications in producing larger water quantities regarding the energy consumption [74-76].

However, membrane processes require skilled personnel to operate it. RO membranes remove all ions present in water, though some minerals are essential for the human body. Therefore, mineral adjustment is sometimes required after treatment, depending on the raw water composition and purpose of water treatment. Fluoride-rich concentrate may also require additional treatment. Membrane application is quite expensive in comparison to other options.

### 1.2.11 Diffusion dialysis

The diffusion dialysis (DD) technique is based on the application of an ion-exchange membrane to transport ions through a membrane. The technique employs only one kind of membrane, cation or anion exchange membrane. The driving force in this technique is concentration difference. It works by supplying a stripping solution on one side of the membrane, while the other side is supplied with the solution to be treated. In fluoride removal, anion exchange membrane (AEM-positively charged membrane) and alkaline stripping solution are usually employed, as it is shown in Figure 1-7. Diffusion of $OH^-$ ions from the stripping solution through the AEM occurs because of the different concentration between the two solutions. Then, as the $OH^-$ ions from stripping solution permeate to the treated solution, electrical potential is generated by the two solutions and act as driving force for the $F^-$ ions in solution to permeate through the membrane to the stripping solution.

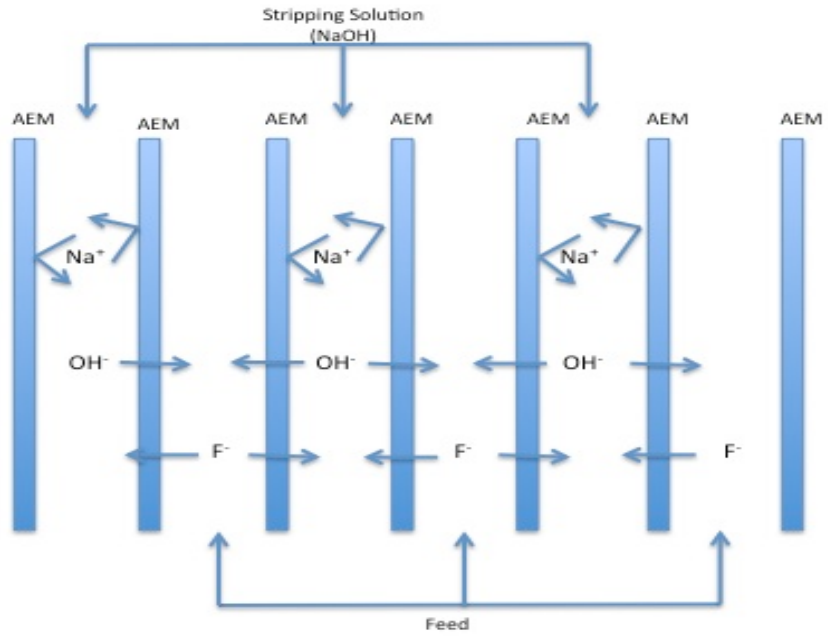


**Figure 1-7 Schematic drawing illustrating the principle of diffusion dialysis using NaOH as stripping solution in a stack of anion-exchange membranes (own work)**

A hybrid of diffusion dialysis with adsorption was proposed to investigate its capability to eliminate excess fluoride in drinking water [77]. Though removing fluoride by DD can be considered as a potential to recover ionic form of fluoride from the concentrated solution, stripping solution in the outlet may lead to another treatment [78]. This treatment is needed

to avoid side problems caused by high fluoride concentrated stripping solution. The removal of fluoride from feed water will be less efficient when the difference in fluoride activities between the two compartments is too low [77]. To avoid the backflow of fluoride ion to the feeding solution, complexation of fluorides with aluminum is necessary if the receiving solution circulates in a batch mode [79].

### 1.2.12 Electrodialysis

Electrodialysis (ED) can be described as membrane-based technique for ion separation, which employs concentration difference as driving force for ion transport under the influence of an applied electrical potential difference. This is done in a configuration called an electrodialysis cell. The cell consists of a feed (diluate) compartment, a concentrate (brine) compartment and an ED Unit. The ED unit is formed by configuration of staples of anion and cation exchange membranes placed between two electrodes. The ED process is illustrated in Figure 1-8.

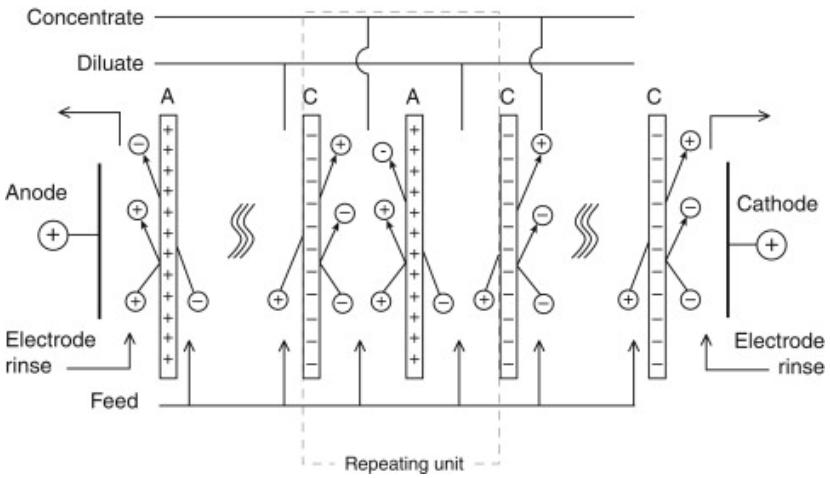


**Figure 1-8 Schematic diagram illustrating the principle of desalination by electrodialysis in a stack with cation- and anion-exchange membranes in alternating series between two electrodes, where A = anode and C = cathode [80]**

The performance of ED as method to reduce fluoride concentration from brackish water and the effect of process parameters and ionic species for fluoride removal using electrodialysis were investigated in previous studies [81,82]. It was concluded that initial fluoride concentration and applied potential are the decisive factors for the increase of fluoride removal. In case of water sources rich in other ions than fluoride, it may cause high

concentration of salt in the concentrated compartment. This becomes an important issue, because it could generate fouling and damage to the membrane [82]. It is also reported that the removal of fluoride was higher in the absence of mono- and bi-valent ions [65].

Due to the relatively high operation cost, this process is not used extensively. The anion and cation exchange membrane are considered as expensive membranes. High operating cost has to be considered if electrodialysis is employed for high rate of ion removal due to intensive use of current. Besides, operators have to be trained for operation and maintenance of the system appropriately.

### 1.2.13 Summary

This review on existing techniques to remove fluoride from drinking water is summarized in the following table as an overview of all techniques.

| Method | Technique | Mechanism | Simplicity | Risk |
|---|---|---|---|---|
| Coagulation and precipitation | Nalgonda | Fluoride is removed through coagulation and co-precipitation of aluminum-fluoride complex | • Established technique<br>• Simple operation<br>• Common chemicals are involved (lime and alum) | • Aluminum and sulfate presence in the product water<br>• Turbidity of fine precipitate<br>• Formation of high volume of sludge<br>• Difficult to control the dosage in case of water sources with different fluoride concentration |
| | Coagulation and precipitation using $CaCl_2$ | Fluoride is removed through precipitation of calcium fluoride | • Simple to medium operation<br>• Less sludge compared to lime<br>• Minimize risk in case of wrong dosage of chemicals compared to Nalgonda<br>• More suitable in industrial application | • Chemicals residue, sludge formation<br>• Turbidity due to fine precipitate<br>• Longer sedimentation time<br>• Could not meet standard limit 1.5 mg/L $F^-$, while higher dosage leads to increased hardness |

| Method | Technique | Mechanism | Simplicity | Risk |
|---|---|---|---|---|
| | Contact precipitation | Fluoride is removed through adsorption of fluoride ion onto bone char and co-precipitation of calcium fluoride and fluorapatite | • Simple operation<br>• Common chemicals (MSP and calcium chloride)<br>• Bone char can be produced using local material (cattle bone) | • Socio-cultural acceptance (Cattle bone, pig bone are unaccepted in several areas)<br>• Chemicals residue need special treatment (phosphate, saturated bone char)<br>• Experiments failed to conclude optimum contact time, so removal capacity and efficiency could not be determined |
| | Electrocoagulation | Fluoride is removed through precipitation of aluminum-fluoride complex. Aluminum is generated through a sacrificial electrode | • Advanced operation<br>• Aluminum needed can be calculated | • Passivation<br>• Low rate of removal when initial fluoride concentration is low<br>• High energy consumption<br>• Experiment failed to conclude reaction, so it is difficult to control the |

| Method | Technique | Mechanism | Simplicity | Risk |
|---|---|---|---|---|
| | | | | process<br>• Presence of sulfate ion decreases the removal efficiency |
| Adsorption | Activated Alumina | Fluoride is removed through adsorption of fluoride ion onto activated alumina surface | • Well known and well established<br>• Medium level of simplicity<br>• No chemicals addition | • Fouling and clogging<br>• Backwash solution |
| | Ion Exchanger | Fluoride is removed through adsorption of fluoride ion onto resin | • Advanced operation<br>• No chemicals addition | • Regeneration solution<br>• Chemicals residue<br>• Low pH<br>• Expensive resin |
| | Bone char | Fluoride is removed through adsorption of fluoride ion onto bone char | • Simple operation<br>• Bone char can be produced using local material (cattle bone) | • Socio-cultural acceptance<br>• Chemicals residue |
| | Bio Sand Filtration (BSF) | Could not be determined | • Local filter medium can be used | • Need pre-treatment<br>• Low or no removal efficiency |

| Method | Technique | Mechanism | Simplicity | Risk |
|---|---|---|---|---|
| Membrane Technology | Reverse Osmosis and Nanofiltration | Fluoride is removed through size exclusion by the porous membrane; different concentration for non porous membrane (RO) | • Advanced operation<br>• No chemicals addition<br>• Process can be controlled | • Membrane fouling shortens the membrane life<br>• Regular backwash required<br>• Needs pretreatment<br>• Because more than 90 % of ions are rejected, product water needs further treatment before consumption (polishing) |
| | Diffusion Dialysis | Fluoride is removed following permeation of fluoride ion in the treated water through AEM to stripping solution by different concentration | • Advanced operation<br>• Fluoride recovery is possible<br>• No chemical addition | • Membrane fouling shortens membrane life<br>• Regeneration solution needed<br>• Chemicals residue needs to be treated |
| | Electrodialysis | Fluoride is removed following permeation of fluoride ion in the treated water through AEM to stripping solution by | • Advanced operation<br>• Fluoride recovery is possible | • Membrane fouling<br>• High energy consumption<br>• Needs intensive pre-treatment to avoid |

| Method | Technique | Mechanism | Simplicity | Risk |
|---|---|---|---|---|
| | | different concentration influenced by electrical potential difference | | membrane fouling because of precipitation |

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# Chapter 2 General Objective and Scope of Study

## 2.1 General objective

The importance to prevent endemic fluorosis cannot be argued. Reducing fluoride concentrations to the permissible level in drinking water is one option to avoid excessive intake of fluoride through drinking water. However, conventional water treatment methods do not remove fluoride ions.

Based on previous works as it is already discussed in chapter 1, it is concluded that each method has its own advantage and drawback. Therefore, further investigations on alternative methods that combine the advantage of each method while at the same time eliminating its drawback are needed. In fact, the problem concerning fluoride-contaminated drinking water is much more relevant in developing countries. Therefore, the alternative methods should allow for a simple operation, be affordable and effective in removing fluoride without causing other problems such as excess of aluminium concentration in drinking water and high turbidity.

## 2.2 Scope of study

This study is focusing on the investigation of several techniques/hybrids for water defluoridation that have not been proposed before or have not yet been studied systematically. Aim of the work is to provide inexpensive and safer alternative methods to the existing ones. To achieve the objectives mentioned above, a review and assessment of fluoride removal methods was carried out as a basis for further work. Each technique in each method category is reviewed based on its principle and its advantages as well as disadvantages. A matrix providing an overview of all techniques is presented as a quick reference at the end of Chapter 1.

Based on the review and assessment, a defluoridation technique via coagulation and precipitation by means of aluminum sulfate and lime is selected as the first method to be investigated in Chapter 4. Though it is already applied in several endemic areas because of its simplicity in operation, especially in India and Tanzania known as Nalgonda technique,

the drawback of an excessive aluminum content in the drinking water that leads to other health risks has not been eliminated. Meanwhile, although this process is already known for a long time, a detailed study of the process chemistry is rarely found. These facts lead to the limitation with regard to its development for a combination with other methods. The experiments were carried out in laboratory scale by using spiked water with fluoride concentration adjustment. The primary research interests were in the effects of operational factors such as solution pH, aluminum to initial fluoride ratio and presence of other ions on fluoride removal from aqueous solutions. The fluoride species distribution diagrams of fluoride in aqueous solutions were also established. The optimum process parameters from Chapter 4 are then used as the standard parameters for the development of proposed hybrid methods in Chapter 5.

Investigation of the hybrid process of coagulation and co-precipitation and sand filtration, with emphasis on the possibility for not only removing fluoride but also removing aluminum residue is carried out in as the first method in Chapter 5. This technique is proposed to exploit the advantage of a combination of coagulation-precipitation with conventional filtration. Since a filtration step is not included in the general Nalgonda domestic unit, filtration using low cost sand filter is proposed to eliminate turbidity and excess aluminum in the product water after coagulation and precipitation step. Though this combination is similar to the classical method for water treatment in most waterworks, its development for removing excessive fluoride concentration has not yet been investigated. Performance of the hybrid method is investigated by studying its removal mechanism and interaction between aluminum-fluoride complexes and filter media.

The second method proposed in Chapter 5 is another hybrid defluoridation technique, namely coagulation and membrane ultrafiltration. This hybrid is developed based on the finding and development from the first method and can improve the filtration step by replacing the conventional sand filter with a membrane filter. Ultrafiltration membranes are expected not only to be sufficient to remove the excess aluminum in product water but also to enhance the fluoride removal. The study is focussing on the investigation of the interaction of water and the membrane itself. This study is very important because it will define the reliability of this hybrid to be operated for long-term fluoride water treatment.

Finally, some general concluding remarks are presented in Chapter 6. The outlook and improvement in the existing and hybrid techniques as well as analytical method for analyzing fluoride is proposed. The following Figure 2-1 illustrates the flow and connection between the chapters.

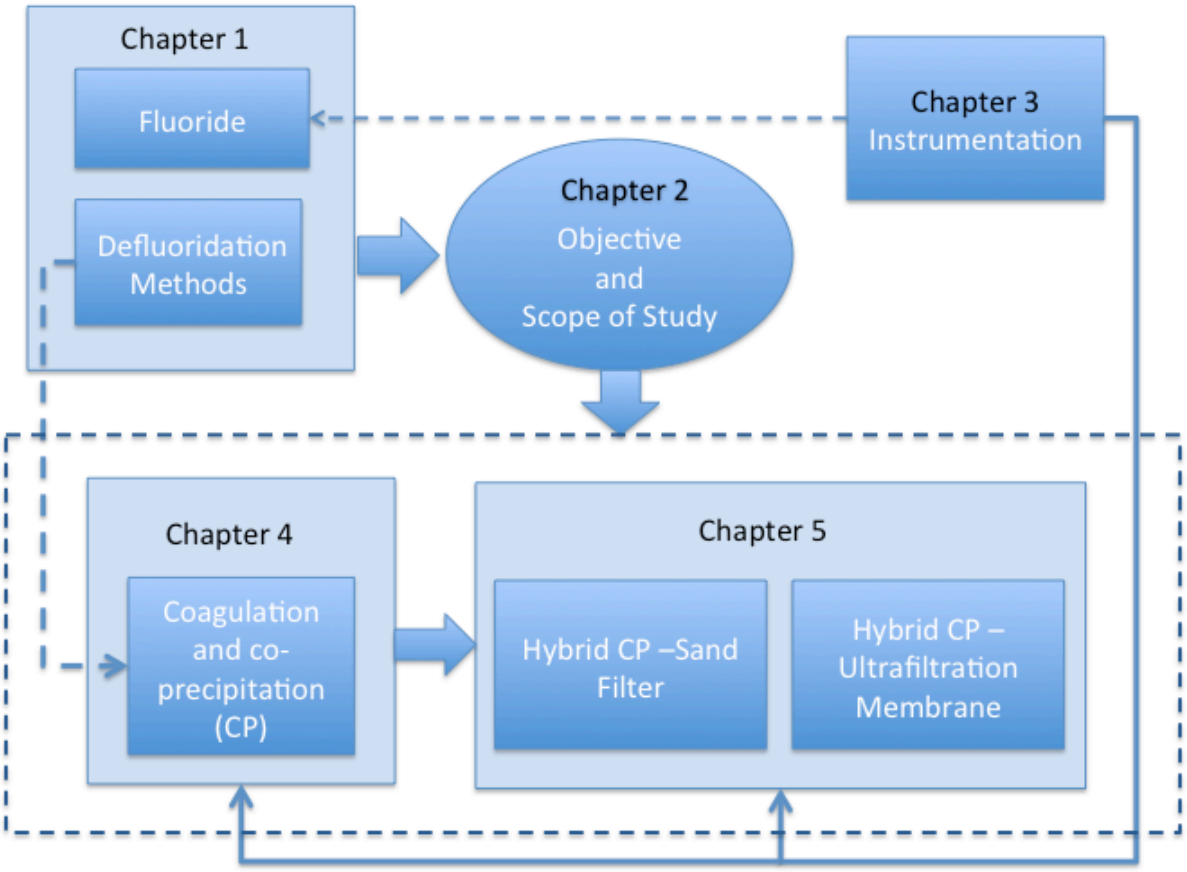


**Figure 2-1 Illustration and the relationships between the chapter in the study**

# Chapter 3 Analytical Instruments

## 3.1 Ion selective electrodes (ISE)

Most of the fluoride data in this study were analysed using an ion selective electrode (ISE METROHM, 781pH/Ion Meter). An ISE is used for direct determination of fluoride ion concentration in water samples. ISE is a potentiometric sensor based on an ion selective membrane. The measured potential refers to the activity of the ion that has to be determined in the sample.

The electrode in ISE uses a crystal of lanthanum fluoride ($LaF_3$) as the selective membrane, where fluoride ions will be mobile. The crystal is doped with europium fluoride ($EuF_2$) to increase its conductivity. When the electrode is immersed in a solution containing fluoride ions, a potential difference develops across the membrane and is measured against a constant reference potential with a standard pH/mV meter. The Nernst equation describes the measured potential as a function of the activity of fluoride ions in solution.

$$E = E_0 - E_J + \left[\frac{RT}{ZF}\right] \ln a$$

where:

$E$ = measured electrode potential in V

$E_0$ = reference potential (a constant) in V

$E_J$ = junction potential in V

$R$ = 8.3145 J/mol. K

$T$ = temperature in K

$Z$ = charge (-1 for fluoride)

$F$ = Faraday's constant = 96,485 C/mol

$a$ = activity of fluoride ions in solution

The ISE responds to the fluoride ion activity, not to the fluoride concentration. According to Nernst's equation, the measurement of equilibrium potential indicates the activity of fluoride ions. The electrode responds only to free ions [1]. It is important to avoid

the formation of complexes that are to be measured because complexation, e.g with aluminium, will decrease the activity. Buffering the sample helps to maintain a constant total ionic strength. Constant total ionic strength prevents a fluctuation in the activity coefficient of the ion being measured because ions have different activity at different ionic strengths, e.g., the activity of $F^-$ at an ionic strength of 0.001, 0.01, 0.1 is 0.975, 0.926, 0.810 respectively [2]. For fluoride analysis a Total Ionic Strength Adjustment Buffer (TISAB) is used. TISAB does not only maintain the ionic strength but also adjusts and buffers the pH value. The solution pH is maintained at 5 where $F^-$ is the predominant species, at lower pH HF (pKa = 3.14) will be dominant. TISAB is usually prepared based on German Institute for Standardization No. 38405-4 (DIN) by dissolving 300 g tri-sodium citrate dihydrate ($C_6H_5Na_3O_7.2H_2O$); 22 g Titriplex IV or 1,2-cyclohexylenedinitrilotetraacetic acid monohydrate ($C_{14}H_{22}N_2O_8.2H_2O$) and 60 g sodium chloride (NaCl) in 1000 mL deionized water [3].

In order to determine the relation between measured electrical potential and concentration of fluoride ions, a calibration is done by varying the fluoride concentrations in standard solutions and measuring the corresponding electrical potential. The standard solutions were prepared of five different concentrations, 0.2, 0.5, 1, 5, and 10 mg/L. The calibration curve is illustrated in Figure 3-1.

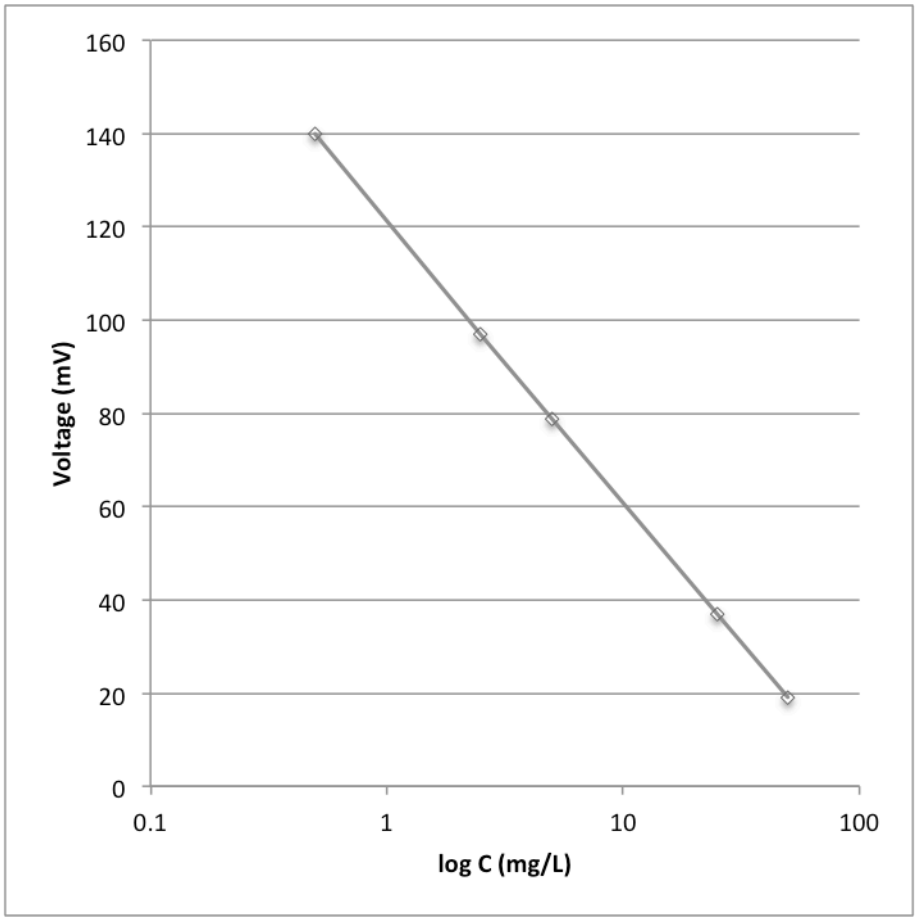


**Figure 3-1 Typical calibration curve of ion selective electrode (METROHM 781ph/Ion meter)** [1]

## 3.2 Ion chromatography (IC)

In this research, ion chromatography (IC-DX500, Dionex with Automated Sampler AS 3500) was used to analyse water samples in order to determine fluoride, chloride and sulfate. The analysis was done by IWW Water Centre Germany. IC is an analytical technique that uses the principle of ion exchange for analyzing anions and cations. It is one type of liquid chromatography that uses an ion exchange resin as stationary phase. The detector in IC will respond and detect the conductivity of the samples.

The first step of ion chromatography is the introduction of sample into a mobile phase. This mixture passes into a column that is uniformly packed with resin fixed with functional group of an opposite charge to the analyte. Fluoride analysis in IC uses a column that contains positively charged active sites (anion exchanger). The most frequently used anion exchanger is based on alkyl chains with ammonium-based functional groups. The two most

important functional groups in anion chromatography are derived from trimethylamine (TMA) and 2-dimethylaminoethanol, (DMEA). The mobile phase, or eluent, is made up of an aqueous solution of salts, e.g., carbonate or bicarbonate salt. Figure 3-2 shows the set-up of s typical IC system.

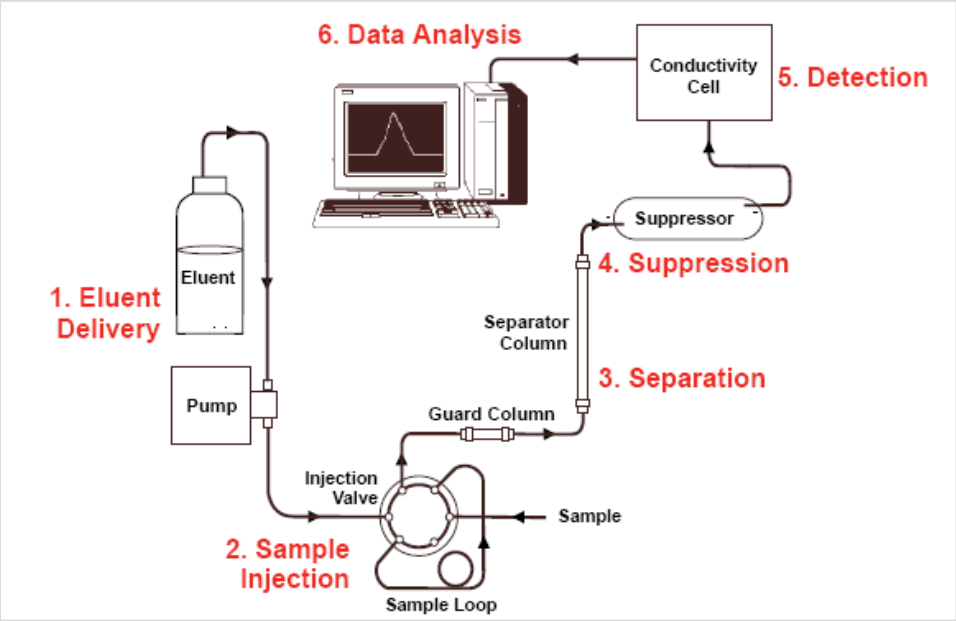


**Figure 3-2 Typical illustration of IC system with suppressor** [4]

A suppressor is technically an anion or cation membrane used to minimize the contribution of mobile phase ions to conductivity by selectively removing mobile-phase electrolyte ions without removing solute ions. The column is placed between the analytical column and the detector. With this suppressor, the IC detector will show only strong conductivity of the solute ion. Figure 3-3 describes typical suppressor operation for anion exchange with $Na_2CO_3$/$NaHCO_3$ as eluent and cation exchange with HCl as eluent.

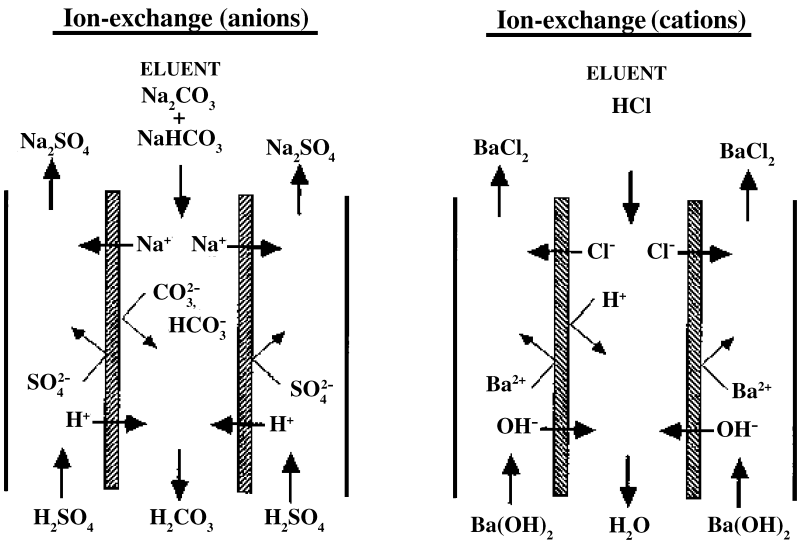


**Figure 3-3 Schematic operation of a suppressor for (a) anion-exchange and (b) cation-exchange separations [5]**

## 3.3 Inductively coupled plasma – optical emission spectroscopy (ICP-OES)

The aluminium analysis for the water samples was mostly conducted also by IWW Water Centre Germany, using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES Varian Vista Pro with axial Plasma and Autosampler SPS 3). ICP-OES is an analytical technique for determining a wide range of elements based on atomic emission. Atomic emission occurs when a valence electron in a higher-energy atomic orbital returns to a lower-energy atomic orbital. Because every element has different energy levels, the emitted wavelength is specific for the respective ion.

The basic operation of ICP is based on a partially ionized gas, typically Argon (Ar), which is less than 1 % ionized in the plasma. The plasma itself is generated in a quartz torch using a 1-2.5-kW radio frequency power supply. Samples are typically introduced into the center of the plasma as aerosols [6].

The atoms and ions present in the plasma are thermally excited. When those atoms and ions are returning to the ground state, photons are emitted. The emitted radiation is spectrally dispersed in a spectrometer and the emission of individual wavelengths is measured with a suitable detector. A scanning monochromator can be programmed to move the monochromator rapidly to an analyte's desired wavelength, pausing to record its

emission intensity before moving to the next analyte's wavelength. The concentration of the elements is determined by comparing emission of sample with the emission of external calibration standards.

In this research, ICP-OES was used to analyse aluminium, calcium and magnesium in water samples. Before the analysis, water samples were pre-treated with acid [7].

## 3.4 Colorimetry (Filter photometry)

In comparison to ICP-OES measurements, aluminium concentrations in water samples were also analysed using the Hach-Lange Schnelltest colorimeter DR/890 method. Every set of Schnelltest Hach-Lange consists of ascorbic acid powder, AluVer 3 reagent powder and bleaching powder. Colorimetry is a photometric analysis technique using a continuous single white light source of which light is passed through a filter for alternative wavelength selection, usually between 400 – 800 nm. When incident light passes through a cuvette containing solution, the intensity of the light leaving the sample will be less than the intensity of light entering the cuvette. In this method, the loss of light is due to the absorption by the compound. Figure 3-4 illustrates the colorimetry principle. Bouguer and Lambert stated that absorption is dependent proportionally on the thickness of the samples if the concentration is held constant. Where $k_1$ is proportionality coefficient and d is sample thickness, absorbance can be formulated as follows (Lambert - Bouguer law):

$$A = k_1 d$$

Beer determined the proportionally of the absorbance with constant layer thickness to the concentration of the absorbing material. This is known as Beer law:

$$A = k_2 c$$

where $k_2$ is a proportionality coefficient and c is the concentration of absorbing material. Combination of these two relations later became known as Lambert-Beer law. The expression can be written as follows:

$$A = \varepsilon_{(\lambda)} c d$$

where $\varepsilon_{(\lambda)}$ is the molar absorption coefficient at λ wavelength (in L/mol cm), c is the concentration of absorbing material (in mol/L) and d is the sample thickness (in cm) [8].

Absorbance can be also expressed as transmittance as a function of light intensity. If $I_0$ is the incident light intensity entering the cuvette and I is the one leaving the cuvette the following relation applies [9]:

$$A = \log\frac{1}{T} = -\log T = -\log\frac{I}{I_0}$$

The instrument is calibrated to 0% transmittance (T) using a shutter to block the source radiation from the detector. After removing the shutter, the instrument is calibrated to 100% T using an appropriate blank. Since the source's incident power and the sensitivity of the detector vary with wavelength, the photometer must be recalibrated whenever the filter is changed.

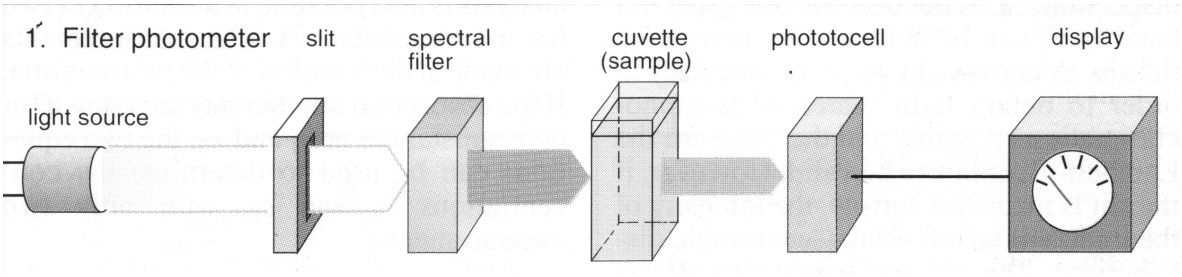


**Figure 3-4 Basic principle of colorimetry [9]**

Because each compound in the visible wavelength range in solution has a typical absorption spectrum, the compound in solution should show predominant colour. For colorimetric analysis of aluminium in this research, Chromazurol-S ($C_{23}H_{13}Cl_2O_9SNa_3$) (Figure 3-5) is used to form a coloured complex with aluminium [10,11]. This reagent will show light pink to dark purple colour when it forms a complex with aluminium. The complex has its maximum absorbance near 540 nm [11].

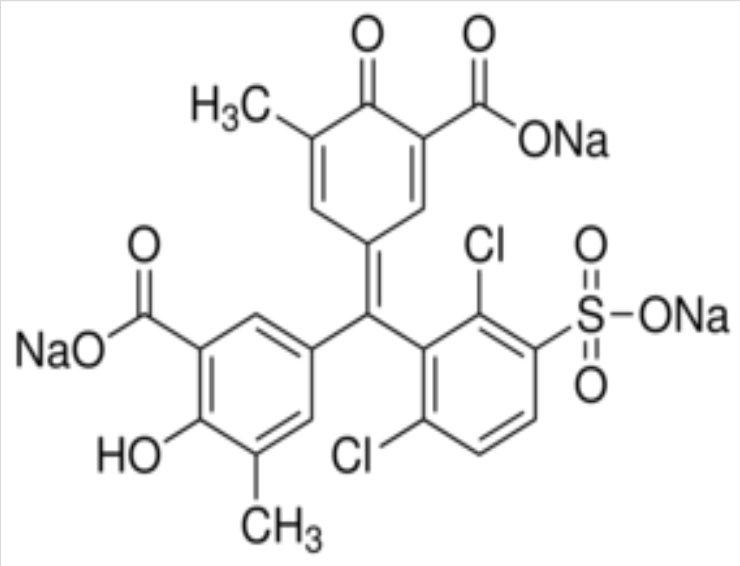


**Figure 3-5 Chromazurol-S or 3-sulfo-2,6-dichloro-3,3-dimethyl-4-hydroxyfuchson-5,5-dicarboxylic acid [11].**

Another common reagent for aluminium determination is aluminon ($C_{22}H_{23}N_3O_9$) (Figure 3-6). Aluminon shows light orange to red colour as complex with aluminium with maximum absorbance near 530 nm [12].

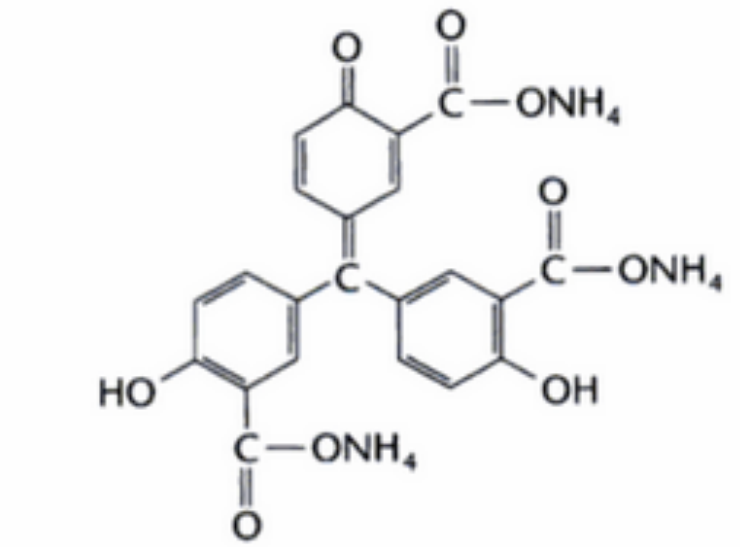


**Figure 3-6 Aluminon or 5-[(3-carboxy-4-hydroxyphenyl)(3-carboxy-4-oxo-2,5-cyclohexadien-ylidene)methyl]-2-hydroxybenzoic acid triammonium salt [13]**

## 3.5 Turbidity analysis

A Nephelometer or turbidimeter was used to analyze the correlation of turbidity and the fluoride removal. Nephelometry measures the amount of light scattered at 90° angles to an incident light beam by particles present in a fluid sample. Only light that passes through absolutely pure water, has relatively undisturbed paths. In a fluid that contains suspended solids, light is scattered by particles present. Figure 3-7 shows the schematic principle of a turbidimeter.

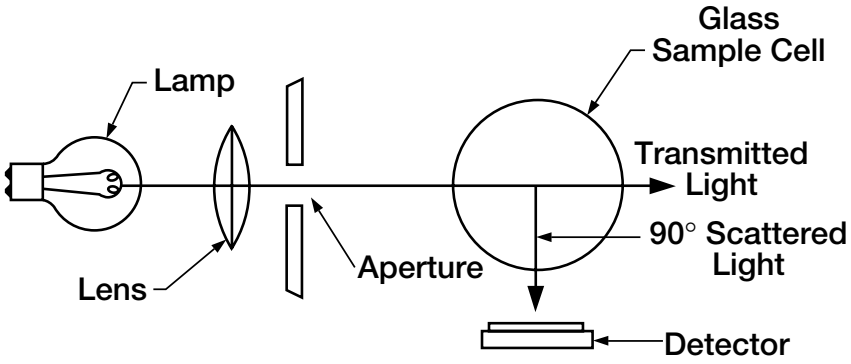


**Figure 3-7 Basic principle of nephelometry [14]**

The pattern of interaction between the sample and light transmitted in a sample containing suspended solid depends on several factors: size, shape and composition of the particles in the solution and to the wavelength of the incident light. The relationship between them can be described by the following equation:

$$I_s = k_s I_0 C$$

where:

$I$ = Intensity of scattered light

$I_0$ = Intensity of source light

$k_s$ = System constant (has to be determined with a calibration curve prepared by using known standard concentration of particles)

$C$ = Solution concentration scattering particles

## 3.6 Element quantification

Energy Dispersive X-ray spectroscopy (EDX) was used to quantify elements retained on the surface of the membrane that was used to enhance fluoride and aluminium removal in this study. The analyses were done by Central Laboratory for Scanning Electron Microscopy, University Duisburg-Essen. EDX spectroscopy is an analytical technique used for qualitative and quantitative elemental analysis of solids and liquids that need only small amount of sample. This technique is categorized as X-ray fluorescence (XRF) spectroscopy.

The fundamental principle of this technique is based on the fact that each element has different X-ray characteristics. When an incident photon with high-energy radiation hits a sample, inner shell electrons of elements in the sample are excited and ejected from the shell. Following the electron ejection, an electron hole is created in the place where the electron escaped. Then, an electron from an outer shell that has higher energy fills the hole. The energy difference between the higher energy shell and the lower energy shell will be emitted as X-ray radiation. Because the energy difference between the two shells of each atomic structure is different, the energy of the X-ray radiation is characteristic for each element. Therefore, the elemental composition of the sample can be measured. As electromagnetic spectrum, characteristic of X-ray can be describe as the following equation:

$$E = \frac{h.c}{\lambda}$$

where:

$h$ = Planck's constant, 6.6254 x $10^{-34}$ J.s

$c$ = Velocity of propagation of light, 3.00 x $10^{8}$ m/s in vacuum

while the wavelength of radiation depends on the atomic number (Z) of the particular element as describe in the following equation:

$$\frac{1}{\lambda} = C(Z - \sigma)^2$$

where:

$C \approx R$ (Rydberg constant, 10973731,43 $m^{-1}$) [15]

$\sigma \sim 1$ (screening coefficient)

In EDX, the emitted radiation is dispersed according to its energy using a semiconductor detector. The X-ray spectrum acquired during the process shows a number of characteristic peaks. The energy of the peaks leads to the identification of the elements present in the sample (qualitative analysis), while the peak intensity provides absolute elemental concentration (quantitative analysis).

## 3.7 References


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# Chapter 4 Coagulation and Co-precipitation for Fluoride Removal using Aluminum Sulfate as Coagulant

## 4.1 Background

Aluminum salts are common coagulants in drinking water treatment. There are several aluminum compounds used for that purpose including aluminum sulfate, aluminum chloride, polyaluminum chloride (PAC), and sodium aluminate. Aluminum sulfate and lime addition was proposed for fluoride removal in drinking water in the USA when fluoride was suspected of causing teeth mottling [1]. As already discussed in chapter 3.2.1, because fluoride concentration in the source of drinking water is high, the dosage of coagulant for fluoride removal is higher than in common drinking water treatment. Later this process was adopted by National Environmental Engineering Research Institute (NEERI) as the Nalgonda technique and developed for low cost treatment used at the community and household level in India. This technique is claimed as easy to be handled and able to remove fluoride in contaminated water up to 90% [2-4].

The Nalgonda technique uses alum, lime and bleaching agent to be added to source water with elevated fluoride concentration. It was suggested that addition of lime is required to maintain the pH [5]. The alum, in this case hydrated aluminum salts, is used as coagulant and a bleaching agent such as calcium hypochlorite powder as disinfectant. Based on the guideline of NEERI the dosages of alum are varying from 145 to 1600 mg/L (16 to 181 mg/L as Al) for treating raw water with fluoride levels of 2 to 8 mg/L at varying alkalinity [6]. Because excessive dosage of aluminum is involved in this process, the pH of the process has to be controlled to avoid elevated aluminum concentration in the water product.

Although it has been widely applied, the removal process in the Nalgonda technique itself is not fully understood because of its complexity [3,7].This study was designed to foster the understanding of the aqueous chemistry for fluoride removal by coagulation and co-precipitation with aluminum sulfate solution as coagulant. The study included the investigation of reaction time of fluoride removal, the effect of aluminum to fluoride molar

ratio, the effect of pH, the effect of the addition of $Ca(OH)_2$ and NaOH to the fluoride removal.

## 4.2 Theoretical considerations

***Aluminum as destabilizing agent***

As coagulant, aluminum salt is a destabilization agent. The destabilization process usually occurs in two ways, namely charge neutralization and sweep flocculation. By **charge neutralization**, positively charged aluminum species from hydrolysis products neutralise negatively charged particles followed by the aggregation of destabilized particles and adsorption of particle. In **sweep flocculation**, the formation of aluminum hydroxide is the main factor, where the growing aluminum hydroxide precipitate enmeshed the particles and colloidal contaminant in the solution. For this reason, excessive dosage of coagulant is usually needed.

***Aluminum complex and co-precipitation of fluoride***

The aluminum ions form a hexaquo complex with water ($Al(H2O)_6^{3+}$), which is often abbreviated as $Al^{3+}$. The water in the hexaquo complex (hydrated aluminum) may undergo exchange reactions with ligands that could be anions or neutral molecules in bulk solution. Hence, in such a complex the anions and neutral molecules are bound directly to aluminum via charge transfer without the presence of water molecule between them. This complexation mechanism is known as **inner sphere complex**. On the other hand, an **outer sphere complex** is formed due to electrostatic interaction between the aluminum and the ligand with the presence of water molecule between them.

Previous studies suggest that the removal of fluoride by aluminum coagulant is a co-precipitation process rather than precipitation [8]. In the case of co-precipitation, fluoride is adsorbed on the surface of $Al(OH)_3$ precipitate. Other study assumed that aluminum-fluoride complexes in the aqueous medium are transformed to form dissolved, colloidal and precipitated forms depending on the solution conditions such as dosage of aluminum salt, pH and fluoride initial concentration [6]. Therefore, these factors play an important role in the fluoride removal but are not independent of each other.

***pH of point of zero charge***

The pH of point of zero charge ($pH_{PZC}$) is an important parameter in fluoride sorption. If the *pH* is equal to the $pH_{PZC}$ the sorbent has an overall neutral charge, above the $pH_{PZC}$ the sorbent becomes negatively charged, and below the $pH_{PZC}$ the sorbent becomes positively charged. Studies have shown that when pH is increased above the $pH_{PZC}$, fluoride sorption decreases due to electrostatic repulsion between the surface and fluoride anions as well as a result of competition with hydroxide ions in solution [9-11]. Reported $pH_{PZC}$ values for aluminum hydroxide are in the range from 6.2 to 9.6 depending upon type, treatment, and hydration of the sorbent [12].

***Effect of pH on aluminum salt in aqueous solution***

Most of the dissolved aluminum is supposed to be present as one of the hydroxo complexes in natural water [13]. Aluminum is easily hydrolyzed in water at pH above 3.5 [14]. When the pH of solution that contains $Al^{3+}$ is raised, dissolved species of $Al^{3+}$ and $(OH)^-$ complex are formed. In case of water containing a high concentration of aluminum, at pH above 6.3 ($K_{s0}$=31.5) $Al(OH)_3$ may start to precipitate. Hydrolysis of aluminum ions is represented as sequence of replacement of the water molecules by hydroxyl ions that can be described as follows: $Al^{3+} \leftrightarrow Al(OH)^{2+} \leftrightarrow Al(OH)_2^+ \leftrightarrow Al(OH)_3 \leftrightarrow Al(OH)_4^-$.

When the fluoride concentration in water is high, aluminum-fluoride complexes will be formed. Water molecules are replaced by fluoride ions as follows: $Al^{3+}$, $AlF^{2+}$, $AlF_2^+$, $AlF_3^0$, $AlF_4^-$, $AlF_5^{2-}$ and $AlF_6^{3-}$. In aqueous environments there are various ligands beside $F^-$, e.g., $SO_4^{2-}$, NOM, $PO_4^{3-}$ that could affect performance of aluminum ions as coagulant. They could substitute stepwise the water molecules to form both soluble and insoluble products that will affect the dose of the coagulant [15].

By using the ChemEQL V3.0 program the aluminum-hydroxyl-fluoride species distribution was calculated. With the input of 3.7 M (or 100 mg/L) aluminum and 0.53 M (or 10 mg/L) fluoride a speciation diagram as function of pH can be generated that is shown in Figure 4-1. Both values are inserted as total concentration in the program calculation, i.e. absence of precipitation is assumed. Then, the program calculates each species concentration as well as the ionic strength of each system at different pH. Finally, these values are used in manual calculation to obtain the species fraction. Complex formation of

aluminum ions with hydroxyl ions and fluoride in aqueous solution is described by the following formation constants:

$Al^{3+} + OH^- \rightleftharpoons Al(OH)^{2+}$ $\log K_f = 9.00$

$Al^{3+} + 2\ OH^- \rightleftharpoons Al(OH)_2^+$ $\log K_f = 17.9$

$Al^{3+} + 3\ OH^- \rightleftharpoons Al(OH)_3$ $\log K_f = 25.2$

$Al^{3+} + 4\ OH^- \rightleftharpoons Al(OH)_4^-$ $\log K_f = 33.3$

$Al^{3+} + F^- \rightleftharpoons AlF^{2+}$ $\log K_f = 7.00$

$Al^{3+} + 2\ F^- \rightleftharpoons AlF_2^+$ $\log K_f = 12.6$

$Al^{3+} + 3\ F^- \rightleftharpoons AlF_3$ $\log K_f = 16.7$

$Al^{3+} + 4\ F^- \rightleftharpoons AlF_4^-$ $\log K_f = 19.4$

$Al^{3+} + 5\ F^- \rightleftharpoons AlF_5^{2-}$ $\log K_f = 20.6$

$Al^{3+} + 6\ F^- \rightleftharpoons AlF_6^{3-}$ $\log K_f = 20.6$

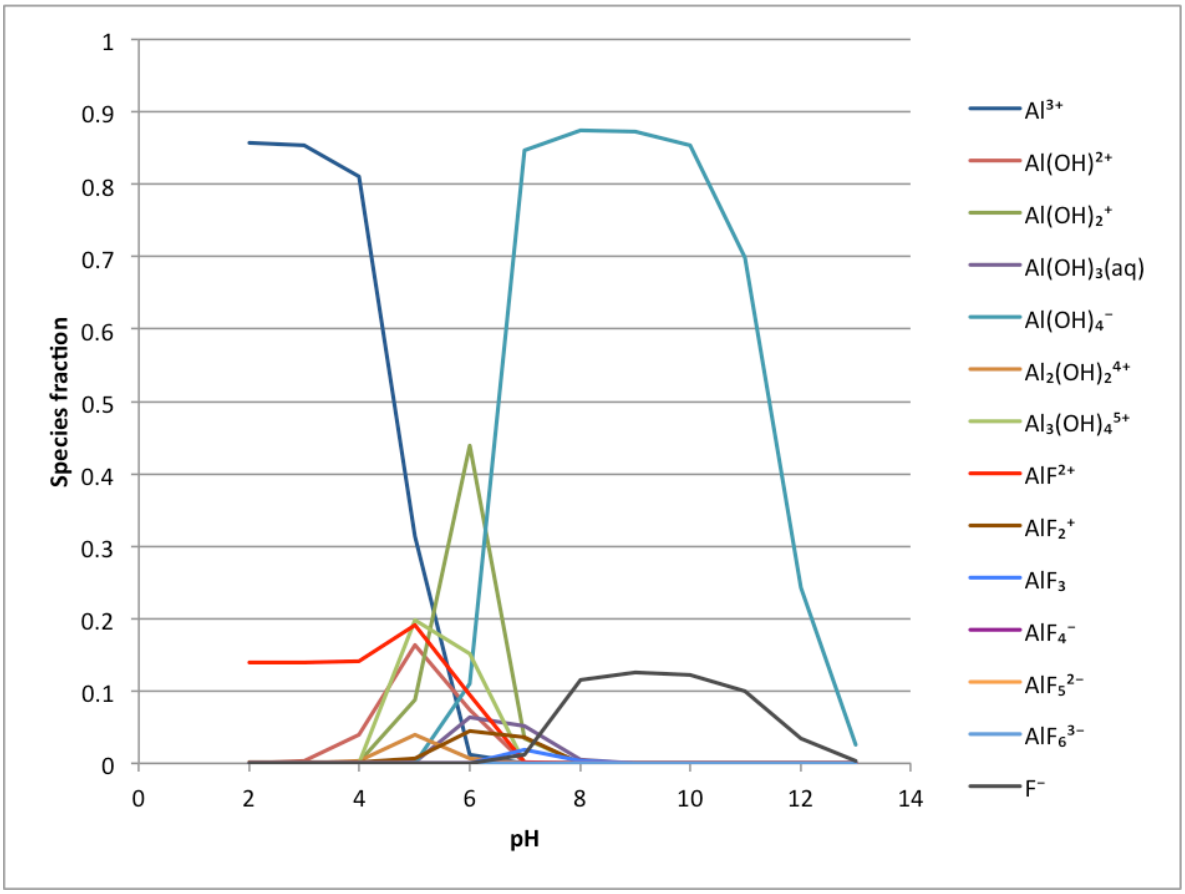


**Figure 4-1 Species distribution of aluminum in solution as function of pH with the presence of [$F^-$] = 10 mg/L and [$Al^{3+}$] = 100 mg/L**

***Effect of $Ca(OH)_2$ on fluoride removal***

$Ca(OH)_2$ is usually used to treat fluoride containing wastewater in the industrial sector because it is considered that producing $CaF_2$ is the least expensive way to remove fluoride from wastewater. This is because fluoride has higher affinity to calcium with bonding energy of 527 kJ/mol compared to other ions, for example to magnesium with 462 kJ/mol [16]. Fluoride reacts with calcium forming $CaF_2$ with a solubility of 0.016 g/L in water. Based on a solubility calculation, it was suggested that in solution where both ions are present in stoichiometric amounts, the fluoride concentration will remain at 8.18 mg/L in solution [17]. However lower fluoride concentration might be achieved in case of excess calcium amount due to common ion effect [17].

## 4.3 Experimental

### 4.3.1 Materials

**Table 4-1 List of materials**

| Chemicals | Suppliers | Purities |
|---|---|---|
| NaF | Merck | $\geq$ 99.5% |
| $Al_2(SO_4)_3.18H_2O$ | Merck | 51% - 59% |
| $Ca(OH)_2$ | IWW | 88.5% |
| Sodium citrate | Merck | 99.0% - 101.0% |
| Titriplex IV | Merck | $\geq$ 99.0 % |
| NaCl | Merck Germany | $\geq$ 99.5% |
| NaOH 1 M | Merck Germany | Standard solution |
| HCl | Sigma Aldrich | 37% |
| $CaCl_2.2H_2O$ | Merck | $\geq$ 98.0% |

***Preparation of solutions***

- Fluoride stock solution with 10 g/L of $F^-$ concentration was prepared by dissolving 22.10 g NaF in deionized water and filling up to 1000 mL.
- Aluminum sulfate stock solution with 10 g/L of $Al^{3+}$ concentration was prepared by dissolving 123.50 g $Al_2(SO_4)_3.18H_2O$ into deionized water and filling up to 1000 mL.
- $Ca(OH)_2$ solution was prepared by IWW with a concentration of 1.7 g/mL of $Ca(OH)_2$.
- TISAB (Total Ionic Strength Adjustment Buffer) was prepared by dissolving 300 g sodium citrate ; 22 g Titriplex IV and 60 g NaCl into deionized water and filling up to 1000 mL [18].
- $CaCl_2$ stock solution with 10 g/L of $Ca^{2+}$ concentration was prepared by dissolving 27.69 g $CaCl_2.2H_2O$ into deionized water and filling up to 1000 mL.
- HCl 0.1M was prepared by diluting 6.2 mL HCl 37% into deionized water and filling up to 1000 mL.

All solutions were stored in PET containers for maximum 1 month.

Most of the experiments were using tap water with typical quality as presented in Table 4-2.

**Table 4-2 Characteristic of tap water used in most experiments (translated from RWW Rheinisch-Westfäliche Wasserwerksgesellschaft mbH: www.rww.de)**

| Parameter Description | Dimension | Median | Low Value | High value | Limit by German drinking water ordinance |
|---|---|---|---|---|---|
| Turbidity | FTU | <0.1 | <0.1 | 0.2 | 1.0 |
| Specific electrical conductivity | μS/cm | 457 | 290 | 582 | 2500 |
| pH value at 20°C | | 7.86 | 7.16 | 8.22 | 6.5-9.5 |
| Calcium | mg/L | 43.7 | 33.1 | 61.9 | |
| Magnesium | mg/L | 7.5 | 5.9 | 9.4 | |
| Sodium | mg/L | 43.3 | 26.0 | 64.7 | 200 |
| Potassium | mg/L | 4.2 | 2.8 | 5.8 | |
| Iron | mg/L | <0.01 | <0.01 | <0.01 | 0.2 |
| Manganese | mg/L | <0.01 | <0.01 | <0.01 | 0.05 |
| Ammonium | mg/L | <0.01 | <0.01 | 0.02 | 0.5 |
| Nitrite | mg/L | <0.01 | <0.01 | <0.01 | 0.5 |
| Nitrate | mg/L | 12.9 | 9.4 | 18.9 | 50 |
| Chloride | mg/L | 49 | 27 | 73 | 250 |
| Sulfate | mg/L | 46 | 32 | 66 | 240 |
| Phosphate | mg/L | 0.14 | <0.10 | 0.34 | 6.7 |
| Fluoride | mg/l | 0.12 | 0.09 | 0.15 | 1.5 |
| Oxygen | mg/L | 7.3 | 3.0 | 13.1 | |
| Total Organic Carbon | mg/L | 0.64 | 0.41 | 0.94 | |
| Arsenic | μg/L | 0.5 | 0.2 | 0.9 | 1.0 |
| Lead | μg/L | <0.5 | <0.5 | 0.5 | 25(1) |
| Cadmium | μg/L | <0.1 | <0.1 | <0.1 | 5 |
| Chromium | μg/L | <0.5 | <0.5 | 0.6 | 50 |
| Nickel | μg/L | 2.2 | 1.4 | 3.3 | 50 |
| Mercury | μg/L | <0.05 | <0.05 | <0.05 | 1 |
| Aluminum | μg/L | 2 | <1 | 9 | 200 |
| Boron | mg/L | <0.10 | <0.10 | 0.12 | 1 |
| Copper | μg/L | 1.6 | <0.5 | 3.7 | 2000 |
| Cyanide | mg/L | <0.01 | <0.01 | <0.01 | 0.05 |

During some experiments, raw water obtained from river Ruhr was also used and spiked with 10 mg/L $F^-$. Afterwards this water will be denoted as Ruhr water. The typical composition of Ruhr water is summarized in table 4-3.

**Table 4-3 Typical composition of river Ruhr water [internal data obtained from IWW Water Centre]**

| Substance | Concentration Range [mg/L] |
|---|---|
| Calcium (Ca) | 35.5 – 45.3 |
| Fluoride (F) | < 0.2 |
| Magnesium (Mg) | 6.5 – 8.6 |
| Phosphate ($PO_4$ ) total | 0.13 – 0.21 |
| Aluminum (Al) | 0.017 – 0.035 |
| Iron (Fe) | 0.062 – 0.093 |
| Manganese (Mn) | 0.025 – 0.037 |
| Dissolved Organic Carbon (DOC) | 1.9 – 2.1 |

### 4.3.2 Experimental methods

***Spiked Ruhr water***

Spiked water was prepared by adding 1.8 mL of fluoride stock solution to 1800 mL Ruhr water and stirred to assure the mixture contained 10 mg/L of $F^-$. Each experiment was performed in 2000-mL jars. To obtain 4 mg/L of fluoride concentration in the water, the same procedure was done with addition of 0.72 mL stock solution.

***Effect of calcium hydroxide on fluoride removal***

To investigate the effect of calcium hydroxide, 4.5 g of $Ca(OH)_2$ solution was added into spiked Ruhr water with 10 mg/L fluoride concentration and was stirred with 250 rpm for 5 seconds. Then, the stirring rate was lowered to 100 rpm for 1 minute and continued by 30 rpm for 4 minutes. After that, the stirrer was turned off and the solution allowed to stand for another 45 minutes to complete precipitation and then 20 mL of supernatant was taken as sample of product water and analysed. This procedure was repeated for experiments with 1.5, 2.25, 3.0, and 3.75 g of $Ca(OH)_2$.

***Reaction time for fluoride removal***

To investigate the reaction time, two experiments were done. The first experiment was prepared by addition of 20 mL NaOH 1M into spiked Ruhr water. Then aluminum sulfate

solution containing 100 mg/L $Al^{3+}$ was added into the system and was stirred with 250 rpm for 5 seconds. Then the stirring rate was lowered to 100 rpm for 1 minute and continued by 30 rpm for 4 minutes. After that, the stirrer was turned off and the solution allowed to stand for another 45 minutes to complete precipitation. 20 mL of sample were taken 5 seconds after addition of aluminum sulfate solution, and sampling repeated after 30 seconds, 1 min, 2 min, 3 min, 4 min, 5 min, 10 min, 20 min, 30 min and 1 hour. The second experiment was done by addition of 4.5 g $Ca(OH)_2$. The further procedure was the same as before but in the second experiment, pH was adjusted to near pH 7.5 by adding concentrated HCl after the addition of aluminum sulfate solution.

***Effect of different working parameters on coagulation and precipitation***

The coagulation and precipitation performance could be affected by several working parameters such as $Al^{3+}$ to $F^-$ molar ratio, pH, $Ca(OH)_2$, and NaOH. In order to investigate these factors, several experiments were conducted with similar working conditions. At the beginning, the spiked Ruhr water was mixed with 4.5 g of $Ca(OH)_2$ (except for NaOH concentration parameter experiment) solution and stirred with 100 rpm for 2 minutes. Then aluminum sulfate solution was added according to Table 4-4 and stirring continued with 250 rpm for 5 seconds. Then the stirring rate was lowered to 100 rpm for 1 minute while pH was adjusted to the designated value by adding HCl or NaOH and stirring was continued by 30 rpm for 4 minutes. After that, the stirrer was turned off and the solution allowed to stand for another 45 minutes to complete precipitation. Then 20 mL of supernatant was taken as sample of product water and analysed.

The following Table 4-4 summarizes the varied experimental parameters.

**Table 4-4 Summary of experimental parameter variation**

| **$[F^-]$ mg/L** | **pH** | **$[Al^{3+}]$ to $[F^-]$ molar ratio** | **$Ca(OH)_2$ g** |
|---|---|---|---|
| 4 | 7.5 | 1; 3; 4; 6; 7; 10 | 4.5 |
| 10 | 7.5 | 5; 6; 7; 8; 11; 13; 14 | 4.5 |
| 10 | 4; 5; 6; 6.5; 7; 7.5; 8; 8.5; 9; 9.5; 10 | 7 | 4.5 |
| 10 | 7.5 | 7 | 1.5; 2.25; 3; 3.75; 4.5; |

| | | | |
|---|---|---|---|
| Reaction time experiments | | | |
| 10 | 7.5 | 7 | No addition of $Ca(OH)_2$ but NaOH 20 mL |
| 10 | 7.5 | 7 | 4.5 |
| NaOH experiments | | | |
| 10 | The pH becomes the variable since it is affected by addition of different volumes of 1 M NaOH | 7 | No addition of $Ca(OH)_2$ but replaced by NaOH 1 M with 0; 5; 10; 15; 20; 25; 30 mL |

### 4.3.3 Analytical methods

All samples were filtered through 0.45 µm membrane filters at the end of each experiment. Filtrates for cation analysis were acidified with 0.1 M $HNO_3$ to near pH 3. The filtrates were analyzed by IWW for total aluminum, calcium and magnesium concentration simultaneously using ICP-OES (Varian Vista Pro with axial Plasma and Autosampler SPS 3). Sulfate and Chloride were also analyzed by IWW using ion chromatography simultaneously with fluoride (IC-DX500 Dionex with Automated Sampler AS 3500).

To determine fluoride concentration, each sample was measured with two methods. The first was ion selective electrode (ISE; METROHM, 781pH/Ion Meter). 50 mL of the sample was taken after each experiment and the fluoride concentration was measured according to DIN 38405(4) with an ISE. To prevent interferences from other ions ($Al^{3+}$, $Fe^{3+}$, etc.), 20 mL of TISAB solution was added to samples. The second measurement method was by ion chromatography (IC-DX500, Dionex with Automated Sampler AS 3500) which was done by IWW. A comparison of fluoride concentrations determined with both methods showed good agreement, indicating that both methods were suitable for fluoride concentration analysis as presented in Figure 4-2.

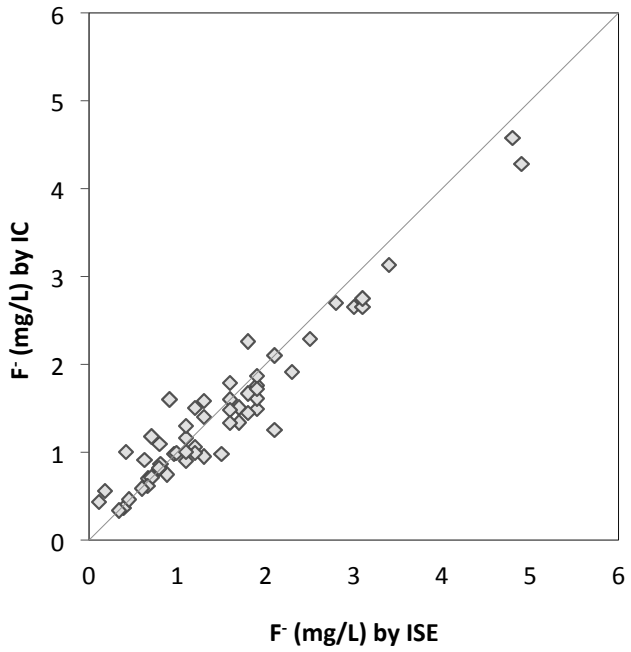


**Figure 4-2 Comparison of fluoride concentrations determined by Ion Chromatography (IC) and an Ion Selective Electrode (ISE) standard deviation : 0.2298 mg/L**

## 4.4 Results and discussion

### 4.4.1 Effect of calcium hydroxide on fluoride removal

The original purpose of the lime ($Ca(OH)_2$) addition into water containing fluoride during the "Nalgonda" process was to maintain the pH [4,19]. Without maintaining the pH, addition of aluminum sulfate solution into the system leads to a decrease of pH into the acidic range. In this condition, aluminum hydroxide is formed in low amount, so there is no precipitation. Thus, co-precipitation of fluoride is also hindered.

In this experiment, the effect of calcium ion was observed by adding $Ca(OH)_2$ to the system. The addition of $Ca(OH)_2$ results in an increase of pH. Different $Ca(OH)_2$ dosages were added to the system as it is shown in Table 4-4. The fluoride concentration decreased from 10 mg/L to approximately 8 mg/L. This is because fluoride has very strong affinity to calcium ions forming fine $CaF_2$ precipitate that has low solubility in water [20]. However, the solubility of fluorite ($CaF_2$) in $Ca(OH)_2$ saturated water is only 2 mg/L and this prevent further removal of fluoride[21,4].

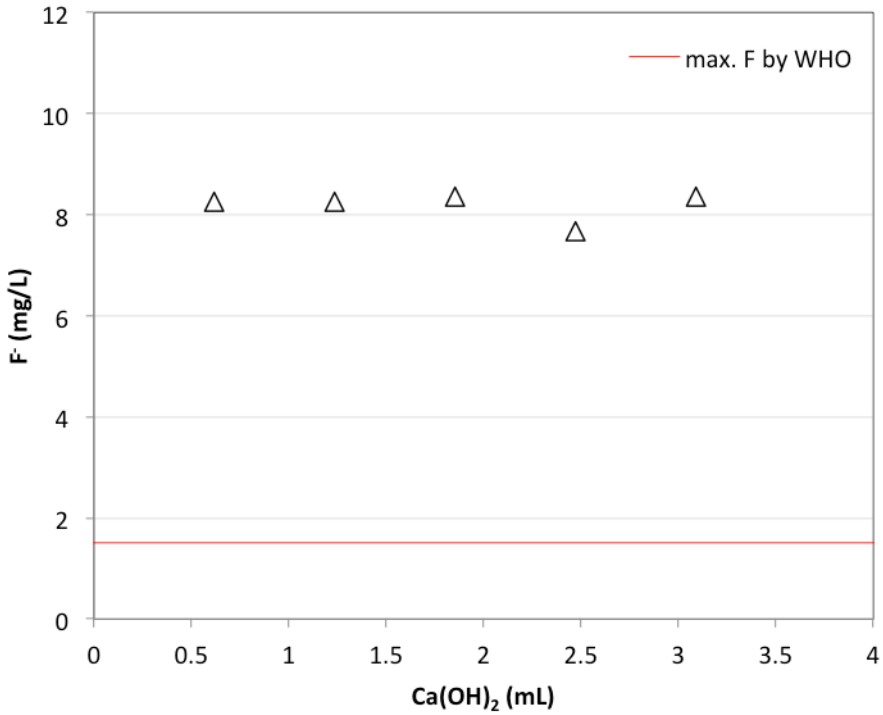


**Figure 4-3 Effect of additional $CaOH_2$ with initial fluoride concentration of 10 mg/L, without additional aluminum sulfate solution to fluoride concentration, pH = 7.5**

### 4.4.2 Effect of sodium hydroxide on fluoride removal

To investigate its effect on fluoride removal, NaOH was added in the system to replace $Ca(OH)_2$. Different dosage of NaOH was added. Without addition of NaOH, system pH decreased to near 4. pH increased along with higher dosage of NaOH. Overall, the result of the experiments was similar to experiments with $Ca(OH)_2$. Fluoride removal was best at the addition of 20 mL NaOH, which corresponds to pH 7.5 as shown in **Kesalahan! Sumber referensi tidak ditemukan.**. Fluoride concentration can be decreased from 10 mg/L to below 1 mg/L.

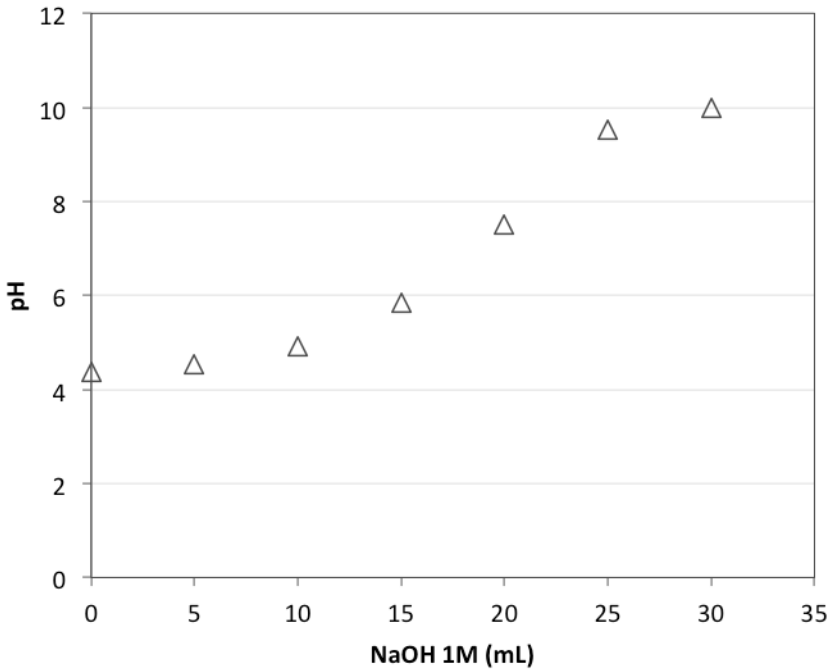


**Figure 4-4 End pH of the system by addition of NaOH as background alkalinity, [$F^-$] = 10 mg/L and $Al^{3+}$ to $F^-$ molar ratio = 7**

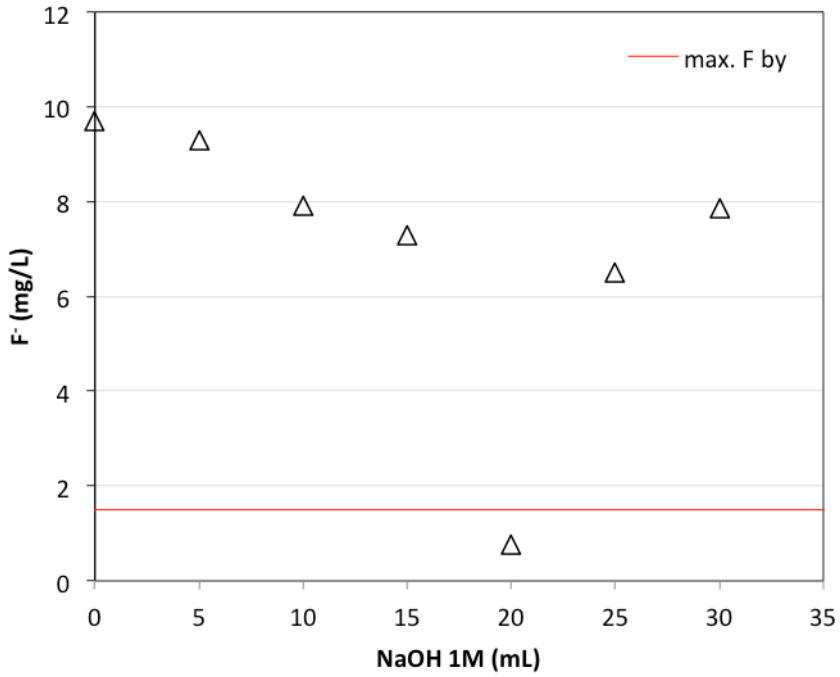


**Figure 4-5 Effect of NaOH on fluoride removal with $F_0$= 10 mg/L and $Al^{3+}$ = 100 mg/L, $Al^{3+}$ to $F^-$ molar ratio 7**

### 4.4.3 Reaction time in fluoride removal

The reaction time experiments were done to ensure the system was at equilibrium state at the end of the experiments. After the addition of NaOH or $Ca(OH)_2$, the system pH increased from neutral pH to pH near 12. Then, $Al_2(SO_4)_3$ was added. The reaction start time was measured when $Al_2(SO_4)_3$ was added. Later pH decreased rapidly because aluminum salt was hydrolyzed as it entered the system and liberated $H^+$. However, the hydroxide ions provided by NaOH maintained the pH at 7.5 even after the addition of $Al_2(SO_4)_3$. While, in the experiments with $Ca(OH)_2$, after $Al_2(SO_4)_3$ was added into the system, HCl had to be added to adjust pH near 7.5.

The result of the experiment, as it is shown in Figure 4-6, indicated that the decrease of fluoride concentration occurs very fast. In both systems with addition of NaOH or $Ca(OH)_2$, the concentration of fluoride in the first 5 seconds decreased rapidly. After stirring was stopped, the fluoride concentration reached the equilibrium state as it is indicated in the result that there was no further significant fluoride removal. Fluoride end concentration in the system with NaOH addition was 1.4 mg/L whereas in the system with $Ca(OH)_2$ addition it was 0.9 mg/L as it is seen in Figure 4-7.

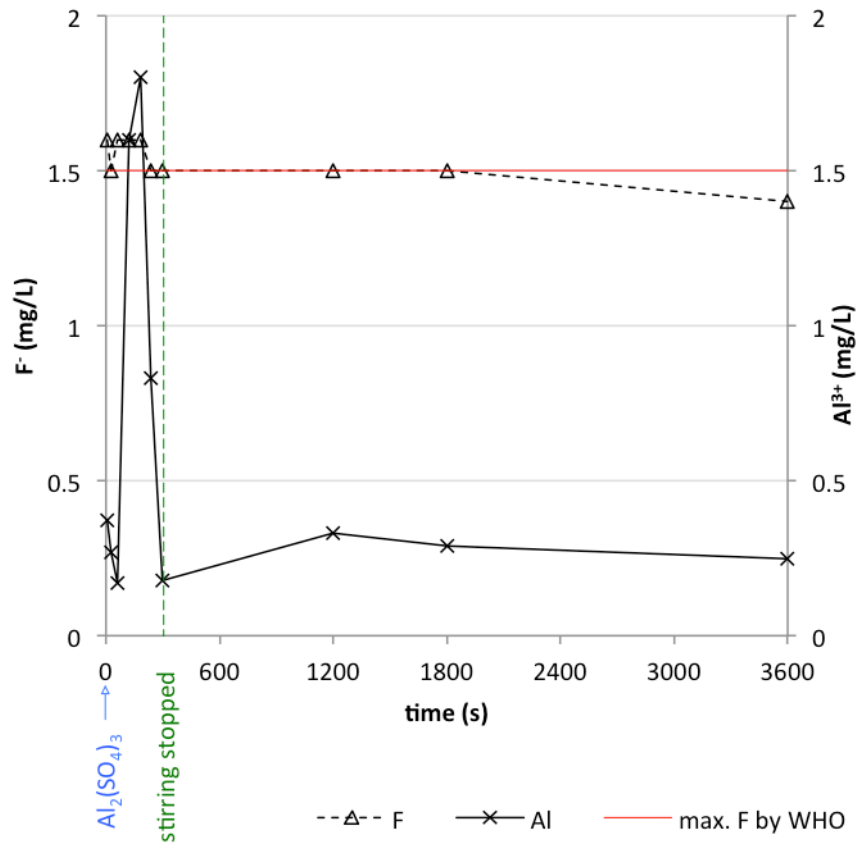


**Figure 4-6 Coagulation of spiked Ruhr water with $F^-$ = 10 mg/L, with addition of 20 mL NaOH 1M as background alkalinity ($Al^{3+}$ to $F^-$ molar ratio = 7. End pH = 7.5)**

The decrease of aluminum in the system with NaOH occurred very fast. This is because the system were reaching equilibrium at pH 7.5 faster than the system with over dosage of $Ca(OH)_2$. The slight increase of aluminum concentration in the system with NaOH during the stirring time is supposed to be the effect of mixing. Meanwhile the increase of the aluminum concentration shown in Figure 4-7 is supposed to be the effect of addition of concentrated HCl in a very short time that causes sudden decrease of the pH. At acidic pH aluminum coordination with water is dominant, especially at pH below 3.5. Afterwards, pH increased along with further mixing. As pH raised, the aluminum coordination with hydroxyl ions and fluoride are more dominant and the corresponding complexes were formed. In this case, aluminum hydroxide precipitate were formed an adsorb fluoride ion which led to the decrease of both the concentration of fluoride and aluminum ion. Considering that the coagulation was done in excess amount of coagulant, so the possible formation of aluminum hydroxide precipitate is very high, the fluoride concentration decrease was very fast and

took place in the neutral pH, it can be concluded that the removal of fluoride was following sweep mechanism[22]. In addition, Figure 4-1 shows the dominant dissolved species at pH between 6 and 8 is $Al(OH)_4^-$. This means that the possibility of removing fluoride ions by charge neutralization is low.

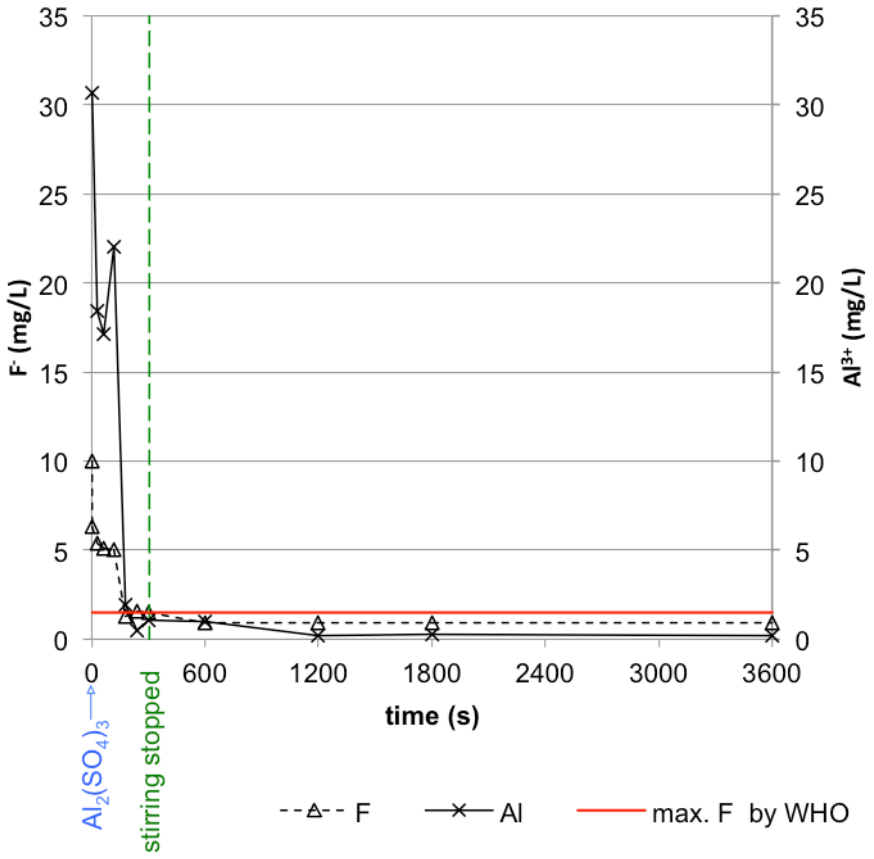


**Figure 4-7 Coagulation of spiked Ruhr water with $F^-$ = 10 mg/L, with addition of 3 mL $Ca(OH)_2$ as background alkalinity ($Al^{3+}$ to $F^-$ molar ratio = 7.0, end pH = 7.5)**

### 4.4.4 Effect of aluminum to fluoride molar ratio on fluoride removal

To investigate the effect of aluminum to fluoride molar ratio on the fluoride removal, different ratios were applied in the experiments. Addition of lime at the beginning of the experiment made the pH to become 12. Then pH was adjusted to 7.5 by adding HCl into the system while it was stirred. Figure 4-8 shows the result of different aluminum to fluoride molar ratios on fluoride removal.

With an initial concentration of 10 mg/L, low fluoride removal can be observed in Figure 4-8 with $Al^{3+}$ to $F^-$ molar ratio = 4, while $Al^{3+}$ to $F^-$ molar ratio $\geq$ 7 that is equal to 100 mg/L

aluminum succeeded to remove 85-96% fluoride, i.e., to achieve the desired fluoride concentration below 1.5 mg/L. A lower amount of aluminum as hydrolysis product leads to lower possibility of complexation with fluoride. A higher molar ratio ensures the higher possibility for fluoride to coordinate with aluminum. However, lower $Al^{3+}$ to $F^-$ molar ratio is favorable because it will decrease the risk of high residual aluminum dissolved and suspended in the product water.

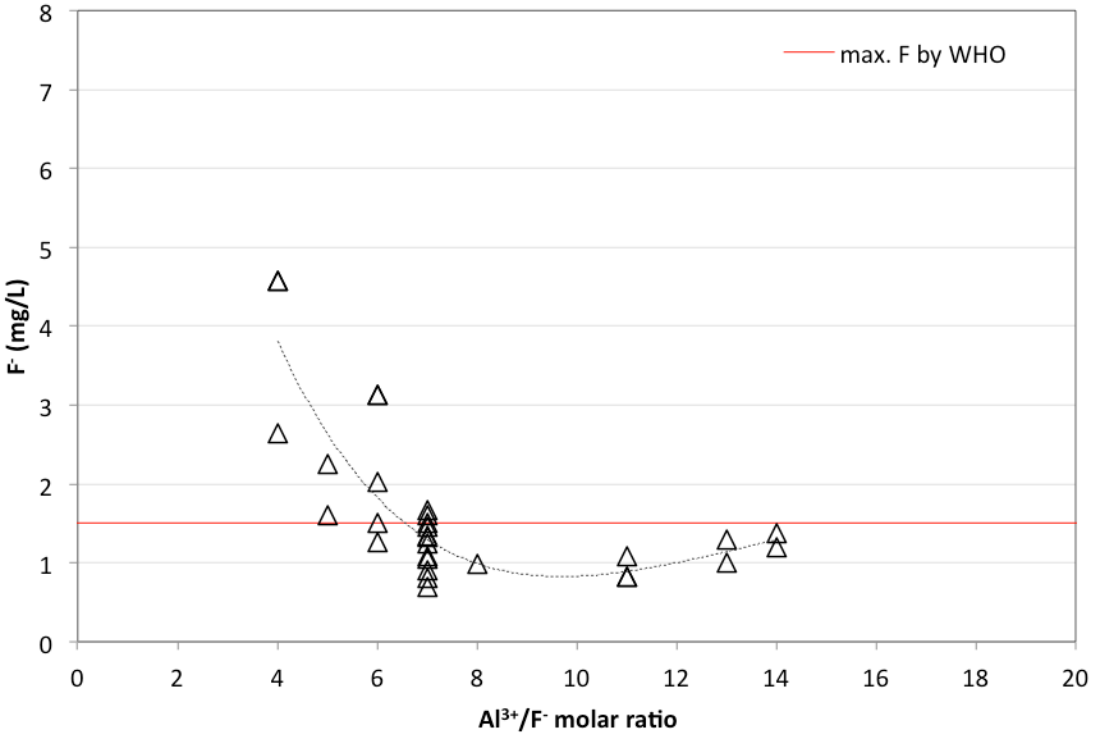


**Figure 4-8 Effect of aluminum sulfate solution dosing on fluoride removal with $F_0$=10 mg/L, at pH 7.5**

The result of the experiment with initial fluoride concentration of 4 mg/L is presented in Figure 4-9. The result shows that fluoride removal to below a concentration of 1.5 mg/L was achieved at a molar ratio $\geq$ 4 that is equal to 17 mg/L aluminum. This means, in such environment where fluoride concentration in water is not tremendously high, less aluminum is needed to remove fluoride. So, this means also, that individual pre-analysis on particular water source has to be done before adding aluminum to remove fluoride in water in order to have an optimum dosage.

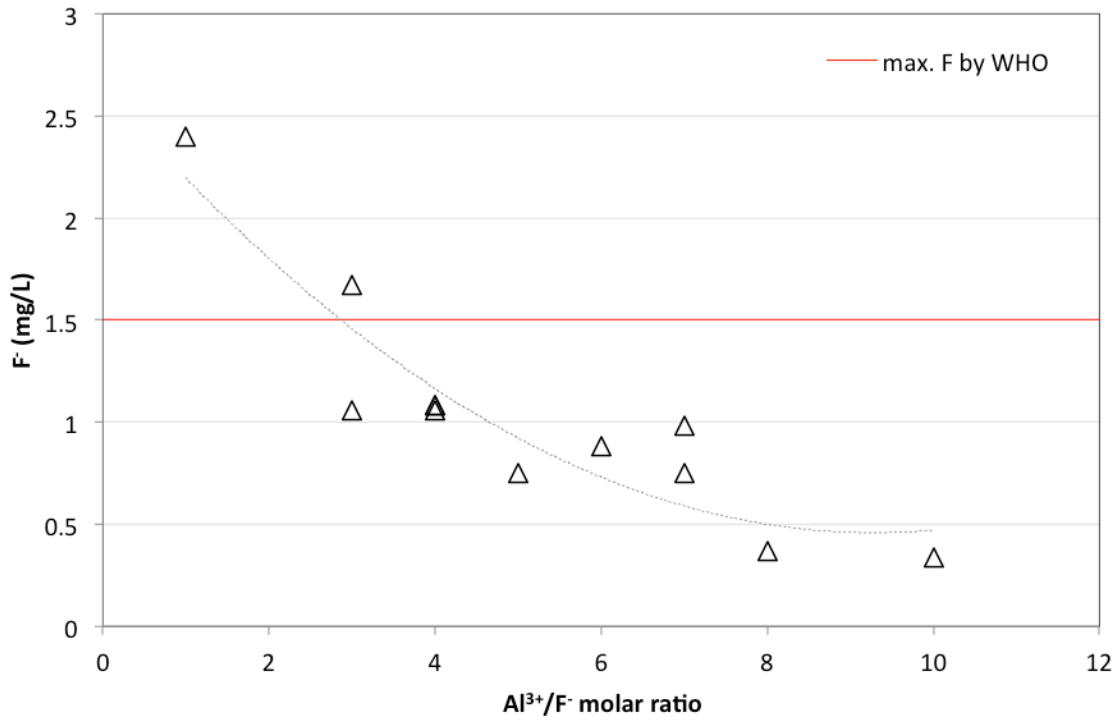


**Figure 4-9 Effect of aluminum sulfate solution dosing on fluoride removal with $F_0$=4mg/L**

### 4.4.5 Effect of pH on fluoride removal

This experiment aimed to investigate the effect of pH on fluoride removal by a series of experiments with different end pH. In the experiments, it was observed that when the $Ca(OH)_2$ entered the system pH raised to 12. The reaction of calcium and fluoride ions was supposed to occur in the system, forming very fine colloidal precipitate. This reaction leads to the decrease of the fluoride concentration in the water from 10 to 8 mg/L, which corroborates the results of previous studies [4,8,21].

As aluminum entered the system, pH decreased fast and was adjusted to 7.5 by adding drops of concentrated HCl while still under stirring. Figure 4-10 shows at pH between 6 to 8, fluoride removal to concentrations below 1.5 mg/L were achieved. However, at pH > 8 fluoride concentration increased again to above 1.5 mg/L.

At pH below 6, the solubility of $Al(OH)_3$ is higher, and the possibility of $Al(OH)_3$ precipitate to be formed is lower than at higher pH. Without formation of $Al(OH)_3$ precipitate, co-precipitation will not occur.

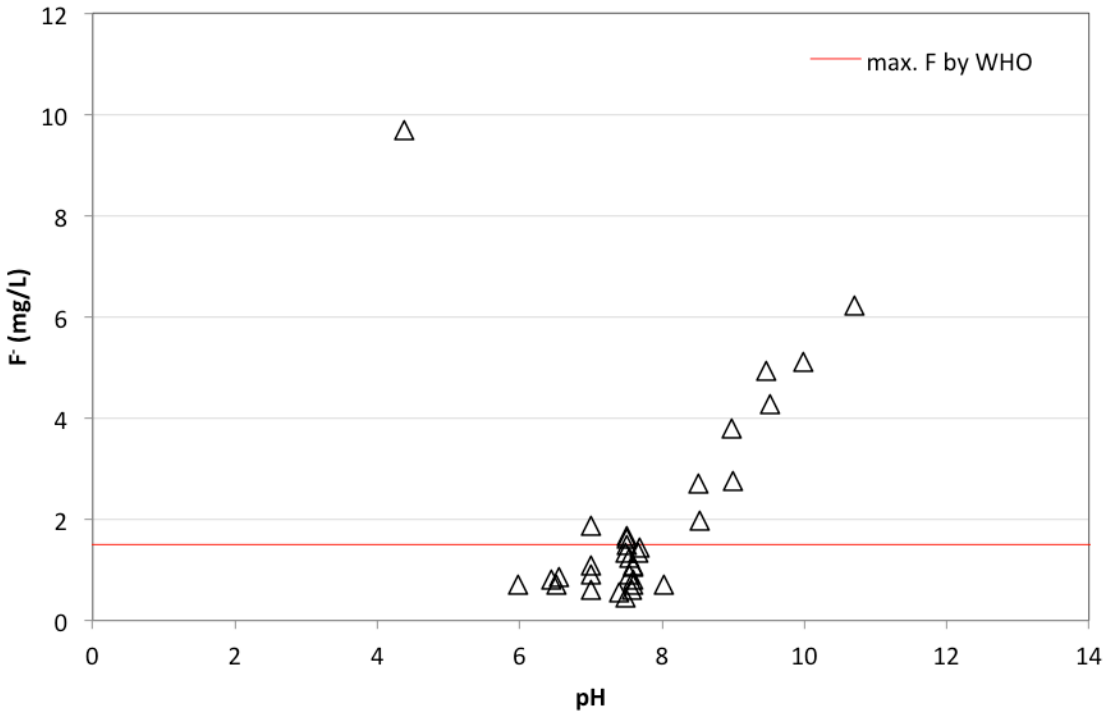


**Figure 4-10 Effect of pH on fluoride removal with initial fluoride concentration of 10 mg/L. $Al^{3+}$to $F^-$ molar ratio=7**

Along with increasing pH between 6 to near 8, hydroxyl ions were present in quite large concentration, which ensures the formation of $Al(OH)_3$ precipitation. In addition, at pH between 6 to 8, $Al(OH)_3$ is below its $pH_{PZC,}$ thus it is positively charged, which supports sorption of the negatively charged fluoride ions by electrostatic interactions. Therefore, at this range of pH between 6 – 8, fluoride removal to concentrations below 1.5 mg/L was achieved.

At pH above 8, the formation of $Al(OH)_4^-$ predominates the system. In addition, the small amount of $Al(OH)_3$ precipitate is negatively charged at pH above its $pH_{PZC,}$ so this leads to repulsion of fluoride ions. Therefore, at pH > 8 fluoride removal is very low with fluoride concentrations increasing with increasing pH and residual fluoride concentrations at the end of the process above 1.5 mg/L.

A previous study found that at the neutral pH below the $pH_{PZC}$ the flocs formed during flocculation are more stable[23]. This result is supported by a previous study on fluoride removal using cake alum, which concluded that the sludge flocs formed around pH 7.1 were much more stable and presented better settling characteristics than in the acidic range of of

6.1 – 6.4 [23]. The more stable the flocs are, the lower the concentration of fluoride ions in the produced water.

By using fluoride and aluminum concentration from the experiments as input data in the mass balance calculation for species calculation, a diagram of species distribution as function of pH can be established as shown in Figure 4-11. The aluminum and fluoride concentrations were inserted as free component in the system, while in Figure 4-1 those values were inserted as total concentration of components. At pH between 4 to 6 $AlF_3$ predominates in the system. At pH near 7 $AlF_2^+$ is the predominant species. This is different from the theoretical calculation in Figure 4-1. At pH > 7, $Al(OH)_4^-$ is the dominant species.

Since fluoride ions were removed mainly by co-precipitation, formation of $Al(OH)_3$ precipitate is very important. At pH between 4-6 there was no formation of $Al(OH)_3$ precipitate. Thus, fluoride removal was very little and fluoride concentration is large in this pH range. The presence of fluoride and aluminum-fluoride complexes in the system changes the equilibrium of the system, thus the species fraction does also change at the specific pH.

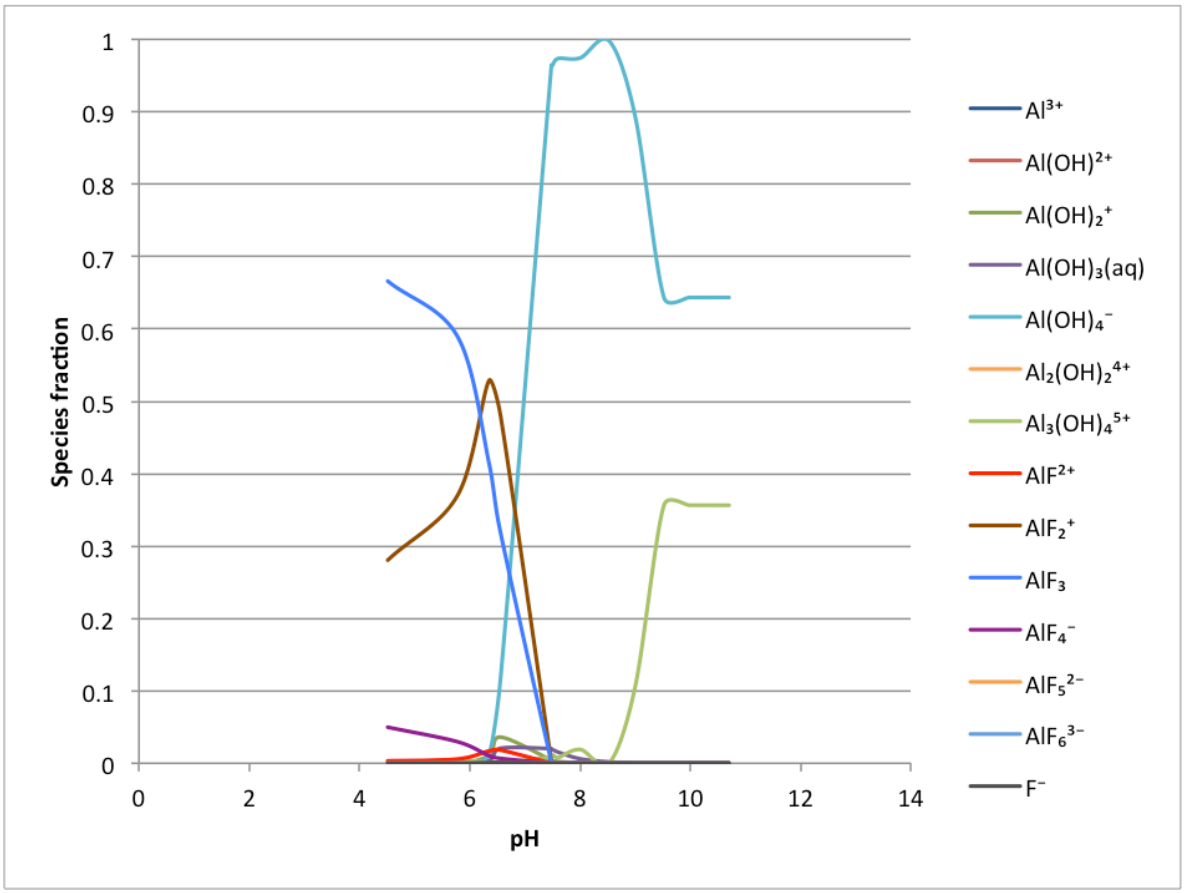


**Figure 4-11 Species distribution of aluminum-fluoride complex in solution as function of pH by using the fluoride and aluminum concentrations from the experiments as input data for calculation using ChemEQL V3.0**

### 4.4.6 Summary

The result of the study on the coagulation and co-precipitation method for fluoride removal using aluminum sulfate solution as coagulant can be summarized as follows:

1. The removal of fluoride occurred very fast. It was best carried out at neutral pH and under excessive amount of aluminum coagulant. Fluoride ions were adsorbed by precipitated aluminum hydroxide. After certain time the precipitated aluminum hydroxide collided and enmeshed the particles and later settled down. It is suggested that the removal reaction follows a sweep mechanism.

2. Reduction of fluoride concentration from an initial concentration of 10 mg/L to below 1.5 mg/L was best at an aluminum dosing of 100 mg/L that is corresponding to an $Al^{3+}$ to $F^-$ molar ratio $\geq 7$. This molar ratio assures a high possibility for fluoride to

occupy the aluminum hydroxide precipitate as adsorption sites. Meanwhile, for fluoride with initial concentration of 4 mg/L, an $Al^{3+}$ to $F^-$ molar ratio $\geq 4$, equal to 17 mg/L aluminum, achieved that purpose. This amount of aluminum is clearly lower than needed in the Nalgonda technique which is 16 to 181 mg/L as Al for treating raw water with fluoride levels of 2 to 8 mg/L. Lower amounts of aluminum are preferred to avoid excess of aluminum residue in the product water and to minimize the sludge formation.

3. The removal of fluoride in raw water from the initial concentration of 10 mg/L to below 1.5 mg/L was achieved in the pH range 6 - 8. At this pH range $Al(OH)_3$ has low solubility and easily precipitates. Besides, at this pH the $pH_{PZCc}$ of $Al(OH)_3$ indicates that the solid is neutral to positively charged. In addition, by maintaining the pH on this level, the amount of $OH^-$ ions as competing ion to fluoride to occupy $Al(OH)_3$ precipitate is also smaller.

4. It can be also concluded that additional $Ca(OH)_2$ serves not only for maintaining pH but also for precipitating fluoride ion. In addition, $Ca(OH)_2$ might also act as the seed of coagulation nucleus.

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# Chapter 5 Hybrid Processes to Remove Fluoride and Excess of Aluminum

## 5.1 Background

After years of experience, the Nalgonda process has been found to have its drawbacks namely elevated aluminum concentration and turbidity in the treated water. In domestic defluoridation design, separation of product water from the precipitate is completed only by the sedimentation process. In some household operation, screen and cloth filters are used after the coagulation step to remove precipitate [1,2]. However, this step cannot eliminate the excess of aluminum because aluminum precipitate is very fine with a diameter of about 10 µm [3]. A previous study found that the residual aluminum content in product water was in the range of 2 to 7 mg/L [4]. This aluminum concentration in product water obviously exceeds the World Health Organization (WHO) drinking water limit, which is only 0.2 mg/L [5].

A high concentration of dissolved aluminum in drinking water is considered to be harmful to the human health [6]. It is presumed that aluminum is a potential neuro-toxicant. Medical research and epidemiological surveys suggest that dissolved aluminum entering the bloodstream may cause Alzheimer disease [7]. It has been reported that $Al^{3+}$, $Al(OH)^{2+}$ and $Al(OH)_2^{+}$ are the most toxic species of aluminum while complexes with fluoride and organic acid such as citric and oxalic acid are less harmful [8,9]. Turbidity in the finished water, another drawback of the Nalgonda technique, occurs because not all precipitate settles down. The very fine precipitates are left in the water as suspended particle. Suspended precipitate cannot easily be removed without adequate separation technique.

## 5.2 Sand filter as a separation method

### 5.2.1 Previous study on “BioSand” filter

A previous study in that context was done to investigate the use of a BioSand Filter (BSF) to remove fluoride as single-step treatment and in combination with the Nalgonda technique. BSF is a modification of slow sand filtration with an active layer on top of the filter. When only a BSF was applied to treat the raw water no significant fluoride removal

occurred. In addition, alternative local materials used as filter media such as local bone char, local lateritic clay, and local brick were rapidly lost its performance that are not suitable for long term application. The study recommended that fluoride removal should be performed as a separate process prior to BSF and conducted preferably by the Nalgonda technique for fluoride concentrations less than 10 mg/L [10]. In some community water works, Nalgonda technique was equipped with sand filter [11]. However, aluminum concentrations after the filtration step have not been investigated.

### 5.2.2 Sand as filter media in waterworks

In most water works, coagulation and precipitation is followed by filtration, usually by a rapid sand filter [6]. This is the simplest hybrid system in water treatment. The sand filter is ensuring that particles not settling in the sedimentation step can be removed effectively. Typically, simple filters use a single type media, which is mostly sand.

***Slow sand filter*** work on low filtration rate between 0.05-0.2 m/h [12]. This process is treating water by two processes. The first is physical treatment such as screening, setling and adsorption and the second is biological treatment. The biological treatment is done by biological growth on top of the sand. ***Rapid sand filter*** work with a greater filtration rate of 5-15 m/h and use a coarser medium, which has higher permeability [12]. This filter treats the inflow water with only physical treatment. It is reported that rapid sand filters are able to remove heavy metals but also, under certain circumstances, phosphorous through chemical precipitation [12]. ***Pressure filters*** are a form of filters that applying pressure to enhance flow the water. It is normally used in the treatment of groundwater that is pumped directly from the borehole into the distribution network for treatment. Flow rates are often in the region of 0.3 – 0.6 m/h

### 5.2.3 Removal mechanism of filter media

There are two major mechanisms of the particle removal in a sand filter, namely ***transport*** and ***attachment***. Transport mechanisms are responsible for providing forces to move particles out of their streamlines onto the grain surface. The suspended particles are transported to the filter material in different ways. This transport mechanism includes ***screening*** when colloidal or suspended particles are retained on the filter bed and this applies to large particles that will not fit to pass the space between filter materials.

***Interception*** occurs when water streamline approach the filter grain so that light particle are intercepted and become attached to filter grain. Heavy particles are usually subject of ***inertia forces*** and ***gravitational settling***, which can be neglected for small particles in the micron size. Small particles are dominantly affected by ***diffusion*** and ***hydrodynamic turbulence*** because their inertia is smaller than hydrodynamic forces in the system.

After being transported, particles that reached the surface of the filter media with diameter of < 1 μm are subjects of surface force [3]. These particles are retained on the surface of the media based on three attachment mechanisms: ***van der Waals*** force is the major attraction force that supports the attraction between filter grain and suspended particle. ***Electrostatic interaction*** occurs when the particles and media surface carry electrical charges, which could be attraction or repulsion forces. The last is ***chemical bridging*** when the attachment is supported by destabilizing agents that lead to the formation of heavy weight polymer that form a 'bridge' between filter grain and suspended particle or between particles [13]

## 5.3 Membrane Process as separation method

As previously discussed in chapter 1, there are several membrane processes that could remove fluoride directly. Reverse osmosis (RO) and nanofiltration (NF) are the most common and widely used membrane processes in defluoridation of water with high fluoride concentration and/or desalination [14-20]. Generally RO is used to desalinate seawater in areas with limited availability of fresh water or on ships. Some researchers [14,17] reported the application of nanofiltration (NF) in defluoridation as an alternative to RO.

The drawback of RO and NF in treating fluoride-rich waters is that up to 99% of the salts in the water are rejected by the membrane, which means not only fluoride will be removed but also other essential salts are eliminated. Besides, the high pressure applied to both types of membrane results in a less cost effective measure, especially if it is designated for less developed areas, which actually comprises most areas of fluoride contaminated drinking water sources.

On the other hand, ultrafiltration (UF) membranes are increasingly applied in advanced drinking water treatment processes, particularly to improve the water quality with respect to organic and microbiological parameters. UF membranes can deliver constant water

quality, show good removal efficiency towards microorganisms, less production of sludge and small size plant compared to conventional treatment plant [21-23]. However, due to its very small size, ca. 0.0001 µm ionic radius, dissolved fluoride ion cannot be removed by UF membranes which usually has pore sizes in the range of 0.1 – 0.01 µm.

Considering that aluminum floc size is 10 µm [3], coupling coagulation and co-precipitation with UF filtration was proposed to be an appropriate treatment not only to remove fluoride in drinking water but also the aluminum residue due to large dosage of coagulant. A previous study on the combination of the precoagulated water using aluminum based coagulant prior to UF membrane process succeeded in minimize the membrane fouling [24]. Other studies on this combination reported that flocs retained on the membrane surface as cake layer could improve membrane performance [25]. However, there is no study yet on this particular combination to remove fluoride.

### 5.3.1 Ultrafiltration membranes characteristic

Ultrafiltration membranes are normally applied in order to separate water from large particles and are characterized by their ability to remove suspended and colloidal particles. They are also known as low pressure driven systems, since high flux can be reached with a pressure difference of 0.2 – 2 bar. UF membranes have a nominal pore size of 0.01 to 0.1 µm [26]. UF is normally used for treating water and wastewater, purifying, concentrating and fractionating macromolecules. UF membranes are also able to remove a large range of materials from water, including fine particle suspensions, colloids, and to retain bacteria, viruses and parasites. Nowadays, UF membranes have become a cost competitive and feasible alternative to conventional methods due to a remarkable decrease in membrane filtration costs enabled by innovations in membrane manufacturing and process conditions [27].

UF membranes show usually anisotropic structures generated in the phase inversion method. They are normally characterized in terms of molar mass (molecular weight) cut–off (limit) instead of particle size (pore size in microns). Nominal molecular weight cut-off (NMWCO) or nominal cut–off is usually defined as the molar mass of a test molecule that would be retained to > 90% by the membrane. Typical NMWCO of UF membranes are in the range of 1 to 200 kg/mol. . The pressure used in UF is usually within the range of 50 kPa - 1

MPa. Among several polymer materials, polysulfone (PS), polyethersulfone (PES), and cellulose–based polymers are usually used for UF membranes. Due to their mechanical strength, thermal and chemical stability as well as excellent film forming properties, PS and PES are frequently used as materials for high performance UF membranes [28].

### 5.3.2 Membrane fouling and concentration polarization

Membrane fouling is one factor that limits the spread of membrane technologies in water treatment plants. Fouling is a deposition of suspended or dissolved substances on external surfaces, at the pore openings or within the pores of a membrane, resulting in loss of performance [29]. Fouling is a result of the interactions between the membrane and solute(s) in the feed and perhaps between the adsorbed solutes and other solutes in the feed stream. Fouling is generally influenced by three factors: membrane properties, solute (solution) properties, and operating parameters [30]. These factors might interact and lead to different effects in different combinations. The presence of inorganic compounds and suspended particles may lead to more complex membrane fouling. Fouling is also strongly influenced by pressure and feed concentration as well as overall equipment design such as temperature and configuration of equipment.

Concentration polarization (CP) is a natural consequence of the selectivity of a membrane that leads to the build-up of the solute concentration near and/or on the membrane's surface. The flux during UF will increase as trans-membrane pressure (TMP) is increased. CP affects the flux by reducing the effective TMP driving force due to the osmotic pressure difference between filtrate and feed solution at the membrane surface. However, after CP reaches maximal point where a gel layer has been formed, the flux will not decrease any more. This phenomenon is inevitable, but it is reversible so that TMP, which also leads to the reduction of fluxes, can be reduced again [31]. Figure 5-1 illustrates the distinction between fouling and CP.

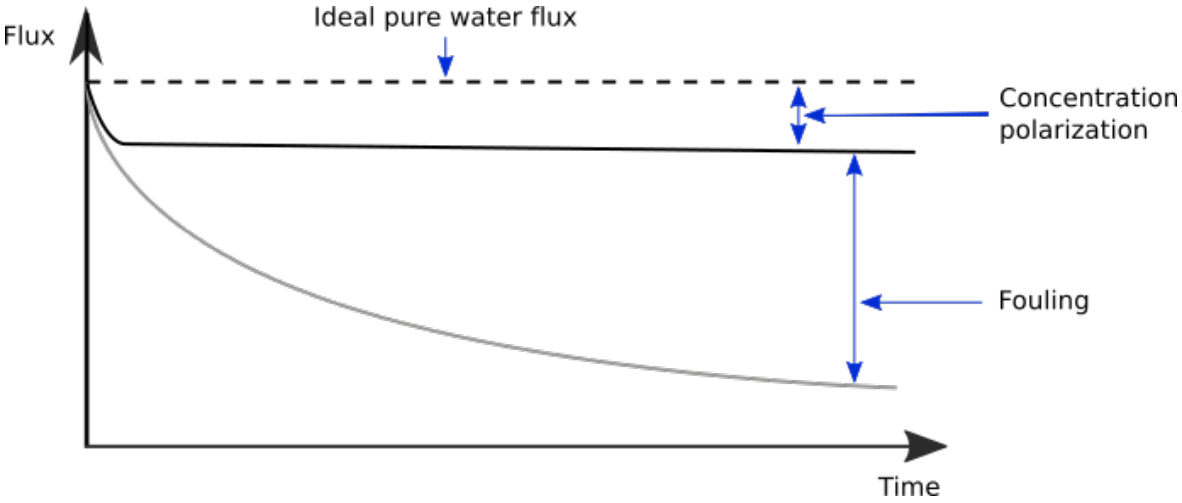


**Figure 5-1 Flux illustration to distinguish membrane fouling and concentration polarization; the solid black line describes the flux with concentration polarization, the solid light grey line describes flux with fouling.**

### 5.3.3 Operation mode of membrane process

There are two different operation modes of the membrane: dead-end and cross-flow as shown in Figure 5-2. In dead-end mode, all feed water passes through the membrane and fouling materials (foulants) are carried to it. It means deposition of material on the membrane surface already begins when the filtration process starts. In cross-flow mode, the major part of the feed water flows tangentially across the membrane surface and only a small part of the flow passes the membrane. Generally cross-flow operation is preferred because the turbulence generated during the operation provides thinner deposits layer and hence minimizes fouling [26].

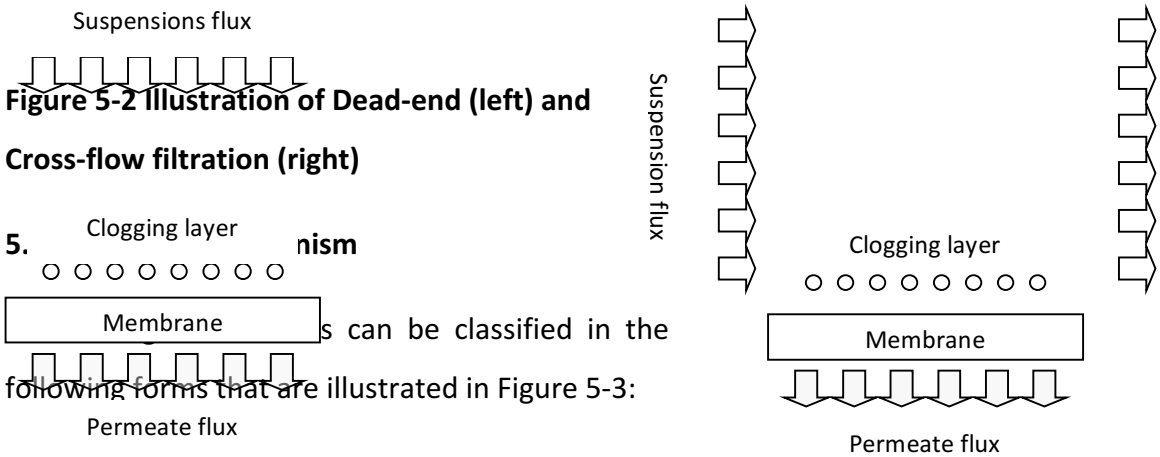


**Figure 5-2 Illustration of Dead-end (left) and Cross-flow filtration (right)**

**5. nism**

s can be classified in the following forms that are illustrated in Figure 5-3:

- **Adsorption**: occurs when attractive interactions between the membrane and the solutes or particles exist. A monolayer of particles and solutes can grow even in the absence of permeation flux leading to an additional hydraulic resistance. If the degree of adsorption is concentration dependent, concentration polarization will exacerbate the amount of adsorption.
- **Pore blockage**: when filtering, pore blockage can occur leading to a reduction of flux due to the closure (or partial closure) of pores.
- **Deposit**: a deposit of the particle can grow layer by layer at the membrane surface leading to an additional hydraulic resistance, which is often referred to as cake resistance.
- **Gel**: the level of concentration polarization may lead to gel formation for certain macromolecules.

**Figure 5-3 Fouling mechanisms of a membrane [31]**

Solute charge, density, hydrophobicity, ionic strength and pH are solution properties influencing the extent and the behavior of fouling. For example, mineral salts can precipitate on the membrane surface because of poor solubility or bind to the membrane directly by charge interactions [30]. In addition, salts can increase the ionic strength, which in turn affects solute–membrane interactions.

## 5.4 Aim of study

This study focused on the removal of aluminum residue in the product water after coagulation and co-precipitation process and proposed two alternatives methods. The first method is hybrid process of coagulation-precipitation and sand filterwith focus on the ability of the sand filter to minimize turbidity and to remove the excess of aluminum concentration to a concentration below the limit set by WHO in drinking water, which is 0.2 mg/L, and for turbidity below 1 NTU. The second method is a hybrid process of coagulation-co-precipitation and UF membrane process with focus on the overall aluminum and fluoride removal ability of the hybrid system. Besides, since fouling is the major factor that limits the application of membrane processes in water treatment, the interaction between the

membrane and product water after the coagulation process was also studied. Experiments were performed in laboratory scale.

## 5.5 Experimental

### 5.5.1 Materials

**Table 5-1 List of materials**

| Chemicals | Suppliers | Purities |
|---|---|---|
| NaF | Merck | ≥ 99.5% |
| $Al_2(SO_4)_3.18H_2O$ | Merck | 51% - 59% |
| $Ca(OH)_2$ | n.a. | 88.5% |
| Sodium citrate | Merck | 99.0% - 101.0% |
| Titriplex IV | Merck | ≥ 99.0 % |
| NaCl | Merck Germany | ≥ 99.5% |
| NaOH 1 M | Merck Germany | Standard solution |
| HCl | Sigma Aldrich | 37% |
| $CaCl_2.2H_2O$ | Merck | ≥ 98.0% |

***Preparation of solutions***

- Fluoride stock solution with 10 g/L of $F^-$ was prepared by dissolving 22.10 g NaF in deionized water and filling up to 1000 mL.
- Aluminum sulfate solution stock with 10 g/L of $Al^{3+}$ was prepared by dissolving 123.50 g $Al_2(SO_4)_3.18H_2O$ in deionized water and filling up to 1000 mL.
- $Ca(OH)_2$ solution was prepared by IWW with a concentration of 1.7 g/mL of $Ca(OH)_2$.
- TISAB (Total Ionic Strength Adjustment Buffer) was prepared by dissolving 300 g sodium citrate; 22 g Titriplex IV and 60 g NaCl in deionized water and filling up to 1000 mL [32].
- HCl 0.1M was prepared by diluting 6.2 mL HCl 37% in deionized water and filling up to 1000 mL.

All solutions were stored in PET containers for a maximum of one month.

***Spiked river Ruhr water***

Spiked water was prepared by adding 4.8 mL of fluoride stock solution to 4800 mL Ruhr water and stirred to assure the mixture contained 10 mg/L of $F^-$. Each experiment was performed in 5000-mL jars.

***Filter media for sand filter***

The filter medium used in this study was sand (European quartz) with an effective size ($d_{10}$, $10^{th}$ percentile of grain diameter) of 0.82 mm and uniformity coefficient ($d_{60}/d_{10}$, with $d_{60}$ meaning $60^{th}$ percentile of grain diameter) = 1.256. The sand filter was set up in a glass column with dimension 4.7 cm diameter and 15 cm length. The sand bed depth was 8.5 cm

***Ultrafiltration membrane***

Commercial polyethersulfone (PES) UF membranes with a nominal cut-off of 100 kg/mol, obtained from Sartorius, Germany were used. The molecular structure of PES is shown in Figure 5-4. By scanning electron microscope (SEM) analysis of the membrane surface and its cross-section, it is shown that the polyethersulfone membrane is a porous asymmetric membrane as it can be observed in Figure 5-5. PES is a thermoplastic polymer that can be used as a membrane for its tolerance to chloride and a wide range of solvents. Figure 5-6 shows the pores and the pore size of the membrane. Variations in pore sizes and pore densities are clearly observed from surface image morphology. The pore and pore size is not uniformly distributed. Regarding its interaction with pure water, this PES membrane is a hydrophilic material, which is easily wettable as seen from its contact angle of 51° for water. This membrane is negatively charged.

**Figure 5-4 Illustration of chemical structure of polyethersulfone [33]**

**Figure 5-5 SEM image of unused PES UF 100 kDa membrane cross-section**

**Figure 5-6 SEM image of unused PES UF 100kDa membrane top surface**

### 5.5.2 Experimental set-up

***Coagulation–co-precipitation step***

The hybrid process was based on a two steps operation set-up, first coagulation–co-precipitation and second filtration and 8 experiments had been performed. The first step parameters were based on the findings discussed in chapter 4 with an optimal aluminum to fluoride molar ratio set to 7 while the pH was adjusted near 7.5.

The first step was conducted in 2 jars with 4800 mL of spiked Ruhr water. Into each jar, first, 3 mL $Ca(OH)_2$ solution that contained 4.5 g $Ca(OH)_2$ were added into spiked Ruhr water and stirred with 100 rpm for 2 minutes. This was followed by addition of 48 ml of 10 g/L aluminum sulfate solution to the system and was stirring with 250 rpm for 5 seconds. Then the stirring rate was lowered to 100 rpm for 1 minute while pH was adjusted to near 7.5 by adding HCl or NaOH and continued by 30 rpm for 4 minutes. After that, the stirrer was turned off and the solution allowed to stand for another 45 minutes to complete precipitation before 100 mL of supernatant was taken as sample of product water and analyzed.

***Filtration step for hybrid coagulation-coprecipitation and sand filter***

The next step was the filtration process. The product water of the previous process was fed into the sand filter. Figure 5-7 shows the diagram of the experimental set up. The filtration flow rate was set to 10 L/h and 12 L/h or equal to 0.57 m/h and 0.69 m/h by applying pump. When the water in both jars reached about 1 cm above the upper top of the precipitation layer, filtration was stopped. Based on the pre-experimental result that after 1 hours of operation, turbidity value had increased, the filtration process was repeated until total product water volume that passed to the filter equal to 1 hour of operation for each experimental batch or ca. 14 L. 20 mL samples for turbidity analysis were taken every 5 minutes. After every batch, the sand in the filter was removed and washed with deionized water until the water that were use to clean the sand show turbidity value of < 0.3. After proper drying, the cleaned sand was used again. The cleaning step was important to assure the reproducibility of data.

**Figure 5-7 Experimental setup of hybrid coagulation-precipitation and sand filter, where M = Motor, Fl = Flow meter, PI= Pressure meter,**

***Filtration with dead-end mode UF flat membrane***

After two containers were filled, product water was flowed to the membrane module and the system was operated for 30 minutes for each experiment. The UF membrane with 100 kDa from Sartorius (PES D=47mm) was used together with a filter holder SM 16 249, Ø 47 mm, $A_{nom}$= 13 $cm^2$. With long body and 200 mL capacity, this holder model permits the flux to flow with a constant profile. Two PTFE screens and a silicon O-ring were used to support the membrane. Instead of compressed air, nitrogen was used, as it is an inert gas to build up the pressure. Nitrogen was pressurized inside the pressure vessels containing the product water by using hoses connected to the filter holder. A pressure gauge was connected to the hose to ascertain that the pressure was set at 0.5, 1.0, 1.5 and 2.0 bars and each experiment was done in triplicate. The filtrate was collected in a pre-cleaned beaker glass and weighted by a digital balance (Kern Compact Balance EW serial number (3000±0.5g). The balance read the data 4-6 times per second and the result was sent directly to the computer. 20 mL sample of filtrate was taken from the beaker glass after the experiment for fluoride and aluminum analysis. The following Figure 5-8 illustrates the experimental set up of the coagulation and UF unit.

**Figure 5-8 Experimental setup illustration of hybrid coagulation and co-precipitation with UF membrane. M = Motorized Stirrer, F = Flow meter, P = Pressure gauge,**

### 5.5.3 Analytical methods

***Fluoride concentration***

To determine fluoride concentration, each sample was measured with ion selective electrode (ISE; METROHM, 781pH/Ion Meter). 20 mL of the sample was taken after each experiment and the fluoride concentration was measured according to DIN 38405(4) with an ISE. To prevent interferences from other ions ($Al^{3+}$, $Fe^{3+}$, etc.), 20 mL of TISAB solution was added to samples.

***Aluminum concentration***

Aluminum concentration was analyzed by using Schnelltest HACH Lange for aluminum test with colorimeter DR/890. This instrument has detection range of 0 to 0.80 and detection limit of 0.013 mg/L for $Al^{3+}$. First, 50 mL sample was taken and the pH being adjusted to pH = 3.5 – 4.5 before being analyzed. Because fluoride complexes and interferes aluminum at all concentration levels, it is necessary to derive the actual aluminum concentration by using the aluminum interference graph shown in Figure 5-9.

**Figure 5-9 Aluminum interference diagram [34]**

***Aluminum, calcium, magnesium and sulfate analysis***

All samples were filtered through 0.45 µm membrane filters at the end of each experiment. Filtrates for cation analysis were acidified with 0.1 M $HNO_3$ to near pH 3. The filtrates were analyzed by IWW for total aluminum, calcium and magnesium concentration simultaneously using ICP-OES (Varian Vista Pro with axial Plasma and Auto sampler SPS 3). Sulfate was also analyzed by IWW using ion chromatography (IC-DX500 Dionex with Automated Sampler AS 3500).

***Turbidity***

Turbidity was measured with Dr. Lange Turbidimeter (Nephla). 20 mL of sample was taken and filled into a cuvette. The turbidity of the samples was read on the display as Formazin Nephelometric Unit (FNU), which is almost equivalent to Nephelometric Turbidity Unit (NTU) with slight differences. Both techniques measure scattered light at 90 degrees from the incident light beam by suspended solid in water sample. However, the FNU is measured with an infrared light source whereas the NTU is measured with white light.

***Characterization of membrane by scanning electron microscopy***

The top surface and cross-section morphologies of the membrane were observed using scanning electron microscope (SEM) by Central Laboratory of Scanning Electron Microscopy, University Duisburg Essen. An environmental scanning electron microscope (ESEM) Quanta 400 FEG at standard high-vacuum conditions was used. A sputter coater K 550 (Emitech, UK) was used for coating of the outer surface of the scan sample with gold/palladium. For cross-section analysis, to maintain the structure, the membrane was broken in liquid nitrogen and sputtered for 1.5 minutes, while for analysis of outer membrane surface, sputtering was done for 0.5 minutes.

***Foulant analysis and material quantification***

Foulant analysis was prepared by drying 1 mg of foulant layer in 120°C oven for 1 hour before being analyzed. Foulant analysis and material quantification was performed during the SEM analysis using DSM 962 with EDX Thermo Electron EDS analysis system Voyager II. Quantification was done using EDX–ZAF, an energy dispersive X-rays quantification analysis

method with ZAF correction that combines the atomic number (Z), absorbance (A) and fluorescence (F) of the element into the calculation.

## 5.6 Results and discussion

### 5.6.1 Aluminum removal of the product water by the sand filter

After coagulation and precipitation, aluminum concentrations were inconsistent between each experiment. The total aluminum concentration was in the range of 0.01 to 0.74 mg/L. As shown in the species distribution diagram in the previous Chapter, on figure 4.1 and 4.9, $Al(OH)_4^-$ concentration is very much affected by pH, especially at pH between 6 and 8. In this pH range, a slight alteration in pH, showed significantly different species distribution. Considering that in daily practical use, feed water will not be buffered, this inconsistent result showed that a further step is obviously needed to assure that aluminum concentrations meet the limit criteria.

The experimental results showed that excess of aluminum were successfully decreased from the water after passing the sand filter to below 0.2 mg/L as shown in Figure 5-10. It is suggested that the decrease of aluminum concentration by passage of the sand filter does not have a linear correlation to the initial aluminum concentration before filtration. It is presumed that aluminum concentration detected in the filtrate water is in the form of aluminum ion with domination of $Al(OH)_4^-$. Because this aluminum species size is very small, screening is the last possibility in the removal mechanism. Therefore, it is proposed that aluminum removal by sand filter was facilitated by chemical bridging where aluminum coagulant formed heavy weight polymer and acted as a 'bridge' between filter grain and suspended particle or between particles. Overall, the concentration of aluminum in the water after filtration meets the drinking water standard.

**Figure 5-10 Total dissolved aluminum concentration of product water before and after filtration step**

### 5.6.2 Further fluoride removal of product water by sand filter

Fluoride concentration at the outlet of the sand filtration process was lower than at the inlet though it was not significant. The result in Figure 5-11 shows that there is no linear correlation between fluoride concentration decrease and its initial concentration in the sand filter process. However, further fluoride removal in the sand filter was supported by aluminum as destabilizing agent. Since aluminum sulfate was used in the previous step as coagulant or destabilizing agent, it can be expected that it facilitated fluoride ion attachment to the filter grain through chemical bridging mechanism.

**Figure 5-11 Fluoride concentration of product water before and after filtration step**

### 5.6.3 Turbidity removal of product water by the filtration step

In the experiments, it was clearly observed that after coagulation and co-precipitation there were suspended particles in product water. Figure 5-12 shows the turbidity trends of the sand filter with flow rate of 10 L/h. The result shows that the sand filter was able to remove turbidity from >1 FNU to below 0.4 FNU. An average of 78% of turbidity has been removed in the system during 60 minutes filtration. After 70 minutes of filtration, water turbidity was increasing.

Meanwhile, with flow rate of 12 L/h turbidity removals were in the best performance in the first 30 minutes, achieving a value below 0.2 FNU, as shown in Figure 5-13. The system was able to remove 72% of turbidity. Overall the results show that the turbidity of the filtrate is < 1 FNU for operation time of 75 – 90 minutes. This result shows that the sand filter has effectively removed the suspended solid.

**Figure 5-12 Turbidity removal by the sand filter, with v=0.57 m/h. The point at 0 minutes represents the turbidity of water before entering the inlet of sand filter module.**

During filtration, removal of suspended particles likely occurs inside the filter bed. Regarding that the aluminum floc size is very small compared to grain diameter of sand filter, interception and diffusion are the dominant transport mechanisms in the removal of turbidity. It is suggested that Van der Waals interaction and charge attraction between suspended solid and the surface of sand grains support the attachment. The positively charged suspended particles are bound to negatively charged quartz sand. Besides that, the coagulation process might still be ongoing before filtration while water stream was flowing in the pipe before it reached the filter. The rest of aluminum coagulant in the water might coagulate the smaller particle facilitated by the shear stress provided by the pump and further encounter chemical bridging.

**Figure 5-13 Turbidity removal by the sand filter, with flow rate = 0.69 L/h. The point at 0 minutes represents the turbidity of water before entering the inlet of sand filter module.**

The increase of turbidity in some of the data points, which is visible in Figure 5-12 and Figure 5-13, might be caused by detachment. At the beginning of filtration, during the attachment, particles were retained and accumulated on the upper grain surface. This layer might collapse because of the hydrodynamic forces due to continuous water flow through the medium. In addition, continuous shear stress generated by the pump also facilitated detachment of particles from filter media. This pressure breaks the attachments and the flocs so the floc size becomes very fine. Those fine particles were not retained by the filter and flowing back to the water stream.

Another possibility includes the phenomenon of sedimentation on the bottom of the filter due to full occupation of upper bed surface by the suspended solid. Because of continuous water flow, this sediment was drifted to the outlet of water flow. This leads to the increase of turbidity after a period time of operation. However, this scenario has to be investigated further because in this experimental set up, it was not possible to collect the suspended solid on the sand filter to compare it with the capacity of the filter.

### 5.6.4 Fluoride and Aluminum removal by UF membrane

The removal of fluoride from the spiked water by coagulation and co-precipitation with aluminum coagulants and UF was first investigated. After 45 minutes of settling time, large particles settled down and could be completely removed from the supernatant. Smaller particles remained unsettled, resulting in a stable suspension. The average fluoride concentration was 1.2 mg/L, while the average concentration of total aluminum residue in the water was 1.6 mg/L. As already discussed in chapter 4, coagulation and co-precipitation process succeeded to remove fluoride to the desired level, however, aluminum concentration is above the drinking water standard. This water was then used as feed in the UF membrane process.

Afterwards, the performance of the ultrafiltration membrane was investigated. Ultrafiltration experiments were conducted in a dead-end batch unit. Collected product water in the container was flown to the UF membrane module and was filtered by UF membrane for 30 minutes. Experiments were done with working pressure of 0.5; 1.0; 1.5; and 2.0 bars and flow rate of 12 L/h. Analysis of the filtrate is shown in Table 5-2.

Compared to the aluminum concentration in the feed, aluminum concentration in the membrane outlet is very low. The result shows that 90% of aluminum concentration was removed by the membrane with average concentration of < 0.2 mg/L. In the case of fluoride, there was further removal by the membrane with working pressure of 1.5 and 2.0 bars. Compared to the fluoride concentration after the coagulation step, there was 25% fluoride removal by the membrane process. There was no remarkable decrease for other ions such as magnesium, calcium and sulfate. Among the investigated conditions, ultrafiltration with 1.5 bars gives the best effect.

The mechanism of fluoride removal during the membrane operation with 1.5 and 2.0 bars was suggested as the effect of the solid layer formed on the membrane surface. Due to pressure and the dead-end mode of operation, the solid layer was formed intensively and this solid layer formed a dense layer on the membrane surfaced. Since 90% of the aluminum was retained on the membrane, this solid layer is able to adsorb free fluoride in the water. Hence fluoride concentration in the water decreased.

**Table 5-2 Ion concentrations in product water after filtration with UF membrane 100 kDa with dead-end mode**

| | Calcium (mg/L) | Magnesium (mg/L) | Fluoride (mg/L) | Sulfate (mg/L) | Total Aluminum (mg/L) |
|---|---|---|---|---|---|
| Feed* | 229 | 8.3 | 1.2 | 538 | 1.6 |
| 0.5 Bar | 229 | 8.3 | 1.2 (SD=0.06) | 537 | 0.15 (SD=0.01) |
| 1.0 Bar | 228 | 8.3 | 1.2 (SD=0) | 536 | 0.17 (SD=0.01) |
| 1.5 Bar | 227 | 8.3 | 0.9 (SD=0.06) | 536 | 0.17 (SD=0) |
| 2.0 Bar | 230 | 8.3 | 0.93 (SD=0.06) | 542 | 0.18 (SD=0.01) |

* Feed = water after coagulation and precipitation

### 5.6.5 Permeate-flux decline of ultrafiltration membranes

Experimental results show there are small deviations in each repetition, however it was the consequence of different surface porosity of each membrane. Such observation is common in membrane technology particularly for experiments with a small membrane area. Similar observations have been reported in a previous study [35]. The results shown in Figure 5-14 are average values with relative standard deviation (RSD) for each flux of 0.0619 bar for 0.5 bar; 0.0611 bar for 1.0 bar; 0.0525 bar for 1.5 bar and 0.0604 bar for 2 bar.

It is evident from results presented in Figure 5-14 that as the working pressure increased, the flux averages were also increasing proportionally. Figure 5-14 also shows that in each operation the flux started at the lower rate and after few seconds, it increased until reaching the maximum. The shape of the membrane holder plays an important role on this profile. With its long body shape, pressurized water needs few seconds to reach uniformly the surface of the membrane. Maximum flux was achieved when pressurized water reached the membrane surface uniformly.

**Figure 5-14 Permeate flux profile of the product water with different pressure operation in the UF filtration steps with dead-end mode by PES UF membrane 100 kDa**

After maximum flux was achieved, flux decreased slightly over time. The decrease of flux indicates that there was an added filtration resistance by the foulant layer. This means, due to its greater size compared to the membrane pore size, the foulant was retained by the

membrane and formed a layer at the membrane surface that, by time, decreased the flux of the water. Besides, at pH above 7, the membrane pores become more negatively charged due to preferential anion adsorption [24]. In this case, anion is less hydrated than cation, and this make anion able to approach membrane surface closely beyond its plane of shear. Thus, the membrane surface acquires negative electro kinetic potential as effect of the anion presence beyong its plane shear[36]. This reduces the membrane pore size, which in turn leads to flux decrease.

**Figure 5-15 Rate of permeate flux decline in the first 100 seconds after maximum flux had been achieved in the UF filtration steps with dead end mode by PES UF membrane 100 kDa**

The experimental results obtained during UF through PES membranes show that membrane fouling was strongly influenced by operational pressure. Figure 5-15 shows the rate of the permeate flux decline after maximum flux had been achieved. Operation with pressure of 1.5 and 2.0 bars generate fast flux decline, while lower pressure with 0.5 and 1.0 bars produced moderate flux decline. After 50 seconds, the flux was relatively stable. The higher pressure resulted in a higher flow rate of filtration. Therefore, more flocs were rejected on the surface of the membrane over time.

A foulant layer supposedly formed faster at the higher working pressure than at the lower working pressure. In addition, the smaller foulant particles generated by shear stress of the higher pressure are able to penetrate into the membrane pore which also caused fouling of the membrane and decrease of flux. This conclusion is supported by the SEM image shown in Figure 5-16. It is shown that the membrane pores cannot be observed because they are covered and filled with white particles. In addition, the polymer membrane will change its structure when it is exposed under pressure. This change in structure leads to flux decline due to lower volume porosity and increased membrane resistance [37].

**Figure 5-16 SEM image of PES UF 100kDa membrane cross-section with deposition of particles over ist surface after being employed for 30 minutes filtration with 2.0 bars with dead-end mode**

Figure 5-16 shows the cross-section of the membrane after being employed for 30 minutes with 2.0 bars of working pressure. Due to the filtration process, the porous membrane supporting section was deformed heavily and blocked by white particles. It can be clearly seen also in Figure 5-17, that there was deposition of white particles on top of the surface of the membrane. This layer leads to the water flux decline during the filtration. Besides, it can be concluded that 2.0 bars of pressure results in a deterioration of the membrane structure.

**Figure 5-17 SEM image of PES UF 100kDa membrane surface after being employed for 30 minutes filtration with 1.0 bar with dead-end mode totally covered with retained white solid substances with 5000 times magnification**

### 5.6.6 Foulant analysis and material quantification of substance retained from membrane surface

Foulant analysis results performed using EDX–ZAF methods are shown in Table 5-3 and Figure 5-18. The largest components by weight in the foulant are oxygen and aluminum. Aluminum and oxygen found in the analysis may come from the aluminum species that were suspended in the water, and aluminum hydroxide fine precipitate that also acts as further adsorption bed of fluoride. This finding may support the proposed formation of aluminum hydroxide as the mechanism of the fluoride removal [38].

**Table 5-3 EDAX ZAF analysis composition percentage of retained substances over the UF PES membrane 100 kDa surface, after being operated for 30 minutes with 2 bar**

| Element | Weight % |
|---|---|
| C | 11.9 |
| O | 56.14 |
| F | 1.44 |
| Mg | 0.22 |
| Al | 24.46 |

| | |
|---|---|
| Si | 1.68 |
| S | 1.95 |
| Ca | 2.21 |
| Total | 100 |

**Figure 5-18 EDX ZAF analysis spectra of retained substances from coagulation and precipitation step over the UF PES membrane 100 kDa surface, after being employed for 30 minutes with 2.0 bars**

The appearance of carbon as a significant component in the analysis is probably originating from the membrane itself since the membrane is formed from polyether sulfone which contains carbon as it is shown in Figure 5-4. Fluoride was also found in a significant amount in the foulant analysis. This shows that $Al(OH)_3$ as the primary layer formed on the surface of the membrane is scavenging fluoride ion and was retained by the membrane. It can be also suggested that this white substances was the fine calcium fluoride precipitate, as calcium was also found in significant value in the analysis. In addition, the presence of calcium might come from the over stoichiometric addition of calcium during the coagulation process. Other components such as silicate and magnesium presumably come from the water itself, while sulfur is presumably derived from the rest of hydrolyzed aluminum sulfate salt as coagulant and from the raw water. Though, sulfur could also originate from the membrane itself since the PES membrane also contains sulfur in its polymer chains. Overall, this foulant analysis result supports the result of water analysis that showed 90% reduction of aluminum concentration from the product water.

Figure 5-19 shows the physical form of the retained substance on top of the membrane surface. The image shows porous white fine substances with irregular shape that totally cover the membrane surface. Compared to the membrane pore size wich is in the range of 0.01 to 0.1 µm (Figure 5-6), the white substance is very small < 0.01 µm. Therefore it can infiltrate the membrane pore and cause an irreversible fouling. Since aluminum-fluoride compound is known to be colorless, the white color is supposed to be coming from the calcium content in the precipitate.

**Figure 5-19 SEM image of the retained substances over the UF PES membrane 100 kDa surface after being employed for 30 minutes with 2.0 bars with 50,000 times magnification**

### 5.6.7 Summary

Based on the result of the investigation, hybrid coagulation and co-precipitation with sand filter shows a meaningful outcome in the laboratory scale. The hybrid process of coagulation and co-precipitation with a subsequent sand filter was successful to decrease aluminum concentration to acceptable concentration with average of 70%. In addition there is unsubstantial further fluoride concentration decrease with average of 13% compared with the concentration before the filtration step. Moreover, the hybrid was also able to remove turbidity with average of 70%. The water turbidity, aluminum concentration and fluoride concentration in the outlet of the sand filter fulfilled the standard set by the WHO. However, application of the hybrid in the field, need to be investigated. Up scaling of sand filter as well as use of higher volume of product water from coagulation step is recommended in future investigations.

Meanwhile, the investigation of hybrid coagulation and precipitation with ultrafiltration membrane was successfully achieved with 90% reduction of aluminum concentration in the water after the coagulation and co-precipitation step by the UF membrane operation. The aluminum concentration after the hybrid process fulfilled the WHO standard of 0.2 mg/L. In the membrane operation with 1.5 and 2.0 bars, there was 25% further fluoride removal compared to the fluoride concentration after leaving the coagulation and co-precipitation process. Overall, the hybrid process assures the fulfillment of the drinking water standard, with fluoride concentrations of < 1.5 mg/L. After 30 minutes of filtration process, the PES membrane structure was already heavily deformed. The surface of the membrane was covered and the pores of the membrane were blocked by the white porous aluminum precipitate. This led to flux decline. Filtration process with operation pressure of 1.5 and 2.0 bars generated stronger permeate-flux decline, while lower pressure with 0.5 and 1.0 bar produced moderate flux decline.

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# Chapter 6 General Conclusion and Outlook

In this work, hybrid techniques as alternative methods in removing elevated fluoride concentration in drinking water resources without causing excess of aluminum concentration and high turbidity in treated water have been evaluated. The study on the ***chemistry of coagulation and co-precipitation of fluoride with aluminum sulfate*** as the basic method for the hybrids has succeeded to achieve its goal to foster the understanding of the aqueous chemistry for fluoride removal. Beyond that, this understanding provides useful information to control the quality of product water especially with intention to avoid elevated aluminum concentration in the product water and to minimize the use of aluminum coagulant in the process. The analysis of the product water showed that 100 mg/L aluminum sulfate were needed to decrease fluoride concentration from 10 mg/L to below 1.5 mg/L, which corresponds to a molar ratio of Al:F of 7:1. For a lower initial fluoride concentration of 4 mg/L 17 mg/L aluminum sulfate were needed to achieve reduction to below 1.5 mg/L, thus a lower molar ratio of 4:1. Both aluminum concentrations are far below previously reported studies, where 16 to 181 mg/L for treating raw water with fluoride levels of 2 to 8 mg/L had been used [1]. Lower amounts of added aluminum are definitely preferable because this will reduce the risk of elevated aluminum in the treated water. In addition it is also betterfrom an economical point of view. However, more different initial fluoride concentrations have to be examined. These data could complete the current finding so a line of corresponding values could be precisely described in a graph. This graph would help in the quick estimation in aluminum dosage to treat different fluoride concentrations in raw water.

Fluoride removal is taking place by co-precipitation. Because this process is very much pH dependent, pH is the most important parameter to govern this process. The removal was mostly depending on the formation of $Al(OH)_3$ that fluoride will co-precipitate with. Neutral pH was the ideal condition for this process, because acidic pH hindered the formation of $Al(OH)_3$, while basic pH enhanced the formation of $Al(OH)_4^-$ species. Species diagrams for a system that contains 10 mg/L fluoride and 100 mg/L aluminum calculated in this study support this. These diagrams also explain the extremely important role of pH on fluoride

concentrations after coagulation and co-precipitation. Controling the pH during the process was the most important finding to control the quality of product water. Subsequent to this work in the future, additional buffer to the system might provide new information for better system understanding because buffering the system will eliminate the effect of other water parameters on pH.

In the core of this thesis***, hybrid process coagulation and co-precipitation with a sand filter*** has been studied to deal with excess residue of aluminum in the product water. In the laboratory scale, the hybrid coagulation and precipitation with a sand filter shows that turbidity can be removed succesfully, while aluminum concentration can be decreased with no linear correlation to its initial concentration. Addition of aluminum sulfate coagulant in excess amount in this system assured the formatlon of chemical bridging as the mechanism of the removal of aluminum residue by the sand filter[2]. The presented study showed that the overall hybrid performance strongly depends on the coagulation - co-precipitation step. Maintaining stable and good coagulation - co-precipitation step will ensure the optimum result of the hybrid. Utilization of activated carbon as filter material in combination with the quartz sand would be an alternative extension to the work because activated carbon was reported to be able to remove dissolved organic aluminum[3]. Furthermore, up-scaling the size of filter and investigating the effect of different water flow rate will be required in the view of technical application in the field.

Finally, ***hybrid coagulation and precipitation with ultrafiltration membrane*** using a dead end mode and PES as membrane material was investigated. Ultrafiltration alone is not able to remove fluoride in water. However, the ultrafiltration membrane was thought to be sufficient to remove colloidal aluminum-fluoride complexes that could not be removed during sedimentation after coagulation and co-precipitation process. This hypothesis was developed based on the aluminum-fluoride complex size[4]. This hybrid is thought to be more cost effective rather than using energy-intensive-RO or even NF that is able to remove fluoride directly because coagulation-UF energy consumption was reported to be lower than NF [5].

Analysis of the product water of the hybrid at laboratory scale confirmed 90% of the aluminum residues from coagulation and co-precipitation process were retained in the

membrane that was operated at several different low pressures (at max. 2.0 bar). The study also demonstrated that lower pressure provided smaller flux declination. It was also concluded that the use of an ultrafiltration membrane assured that removal of aluminum and turbidity met the limit set by the WHO.

Using different membrane material such as ceramic membrane would be an alternative in the future investigation to find a more durable membrane material for sustainable use. After all, despite this hybrid is quite hard to be practiced in household level, its application in the water works at small community level or in small-scale industry that deals with fluoride containing wastewater would be an interesting task in future studies.

## 6.1 References

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(2) Faust, S. D.; Aly, O. M. *Chemistry of Water Treatment*; CRC, 1998.
(3) Polasek, P.; Muti, S. Cationic Polymers in Water Treatment: Part 1: Treatability of Water with Cationic Polymers. *Water SA* 2002, *28* (1), 69–82.
(4) Ives, K. J. Filtration of Clay Suspensions Through Sand. *Clay Minerals* 1987, *22* (1), 49–61.
(5) Machenbach, I. Drinking Water Production by Coagulation and Membrane Filtration, Norwegian University of Science and Technology, 2007, pp 1–250.

# List of Abbreviations

| | |
|---|---|
| Å | Ångström |
| AEM | Anion Exchange Membrane |
| $A_{nom}$ | Nominal filtration area |
| aq | Aqua |
| BET | Brunauer–Emmett–Teller |
| BSF | BioSand filter |
| C | Celcius |
| CC | Calcium chloride |
| cm | Centimeter |
| CP | Concentration Polarization |
| D | Diameter |
| DD | Diffusion Dialysis |
| DIN | Deutsches Institut für Normung |
| DMEA | Dimethylaminoethanol |
| DOC | Dissolved Organic Carbon |
| E | Energy |
| EC | Electrocoagulation |
| ED | Electrodialysis |
| EDX | Energy Dispersive X-ray |
| ESEM | Environmental Scanning Electron Microscope |

| | |
|---|---|
| FAP | Fluorapatite |
| FNU | Formazin Nephelometric Unit |
| FTU | Formazin Turbidity Unit |
| g | Gram |
| h | Hour |
| HAP | Hydroxyapatite |
| HF | Hydrogen fluoride |
| IC | Ion Chromatography |
| ICP-OES | Inductively coupled plasma – optical emission spectroscopy |
| ISE | Ion Selective Electrode |
| K | Kelvin |
| kDa | Kilodalton |
| kg | Kilogram |
| KJ | Kilo Joule |
| kW | Kilo Watt |
| L | Litre |
| M | Molar |
| Max. | Maximal |
| MF | Micro Filtration |
| mg | Milligram |
| μγ | Microgram |
| min | Minutes |

| | |
|---|---|
| mL | Mili litre |
| μμ | Micro meter |
| MSP | Monosodium Phosphate |
| mV | Milli volt |
| n.a. | Not applicable |
| NEERI | National Environmental Engineering Research Institute |
| NF | Nano Filtration |
| nm | Nano meter |
| NMWCO | Nominal Molecular Weight Cut-Off |
| NTU | Nephelometric Turbidity Unit |
| PAC | Polyaluminum chloride |
| PES | Polyethersulfone |
| PET | Polyethylene terephthalate |
| PS | Polysulfone |
| PTFE | Polytetrafluoroethylene |
| pzc | Point of Zero Charge |
| RO | Reverse Osmosis |
| rpm | Rotation per Minute |
| RSD | Relative Standard Deviation |
| S | Second |
| SD | Standard deviation |
| SEM | Scanning Electron Microscope |

| | |
|---|---|
| TISAB | Total Ionic Strength Adjustment Buffer |
| TMA | Trimethylamine |
| TMP | Trans-Membrane Pressure |
| TX | Texas |
| UF | Ultra Filtration |
| USA | United States of America |
| V | Volt |
| WHO | World Health Organization |
| XRF | X-Ray Fluorescence |

## List of Publications

Publications in peer-reviewed journals

-

Poster presentations

- Lestari, R. B.; Schmidt, T. C. Observation of Fluorosis Cases in Several Volcanic Areas in Java Island; 127. GDNÄ Versammlung, Göttingen, 2012
- Lestari, R. B.; Liu, Y.; Nie, Y.; Wermeckes, B.; Schmidt, T. C. Fluoride Removal From Drinking Water with Electrocoagulation by Employing Al-Pt Electrodes, 243rd ACS National Meeting & Exposition, San Diego, 2012
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Oral presentations

- Lestari, R.B.,“Raising Awareness Concept on Water Pollution Issue in Upper Citarum River”, presentation at DAAD – ITT Alumni Seminar, 4 -10. Nov.2007 in Vientiane, Laos

## Curriculum Vitae

**Der Lebenslauf ist in der Online-Version aus Gründen des Datenschutzes nicht enthalten.**

## Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit mit dem Titel

„Defluoridation of drinking water by hybrid coagulation and filtration process ”

selbst verfasst und keine außer den angegebenen Hilfsmitteln und Quellen benutzt habe, und dass die Arbeit in dieser oder ähnlicher Form noch bei keiner anderen Universität eingereicht wurde.

Bremen, 08 December 2016